APPENDIX B

FIELD EQUIPMENT INFORMATION

Iron, Total

✔Method 8008

FerroVer® Method*

Powder Pillows or AccuVac® Ampuls

(0.02 to 3.00 mg/L)

Scope and Application: For water, wastewater, and seawater; digestion is required for determining total iron; USEPA approved for reporting wastewater analysis**

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* Adapted from *Standard Methods for the Examination of Water and Wastewater*

** *Federal Register*, June 27, 1980; 45 (126:43459)

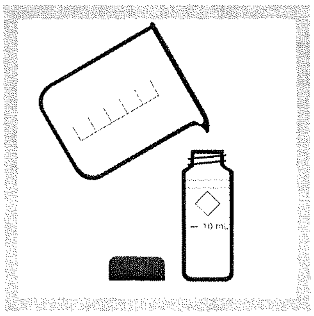
Tips and Techniques

- Digestion is required for determining total iron for EPA reporting purposes. See *Section 4* on page *63* for the digestion procedure.
- For more accurate results, determine a reagent blank value for each new lot of reagent. Follow the procedure using deionized water in place of the sample. Subtract the reagent blank value from the final results or perform a reagent blank adjust. See the instrument manual for more information on *Running a Reagent Blank*.
- After adding reagent, an orange color will form if iron is present.
- Accuracy is not affected by undissolved powder.

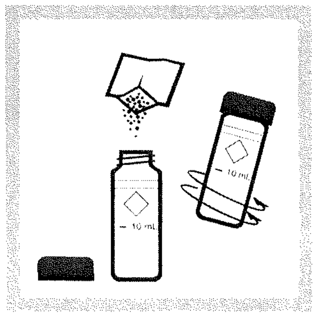
Powder Pillows Method 8008

Hach Programs

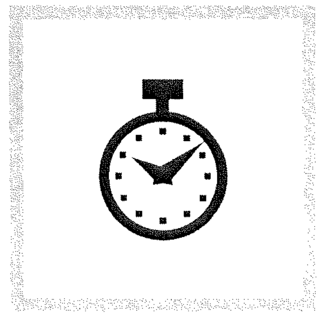
1. Touch **Hach Programs**. Select program **265 Iron, FerroVer**. Touch **Start**.



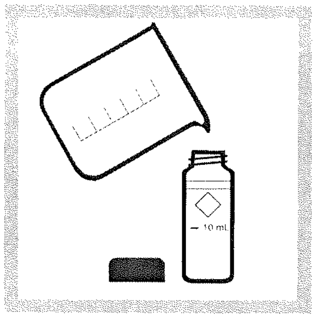
2. Fill a clean, round sample cell with 10 mL of sample.



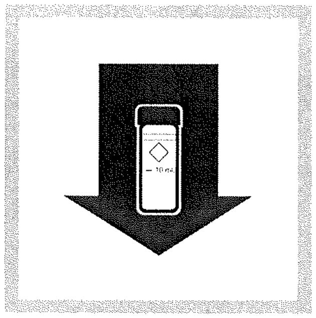
3. Add the contents of one FerroVer Iron Reagent Powder Pillow to the sample cell (the prepared sample). Swirl to mix.



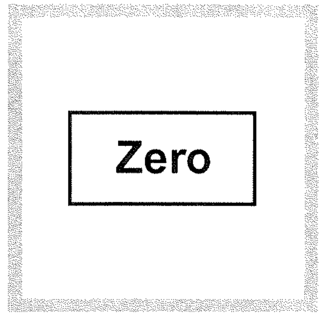
4. Touch the timer icon. Touch **OK**. A three-minute reaction period will begin. (Allow samples that contain rust to react for at least 5 minutes.)



5. Fill another sample cell (the blank) with 10 mL of sample.



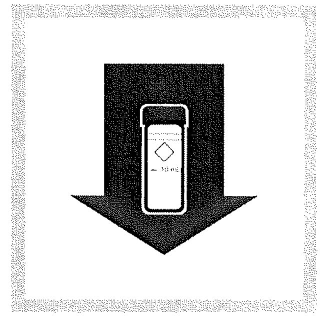
6. When the timer beeps, place the blank into the cell holder.



7. Touch **Zero**.

The display will show:

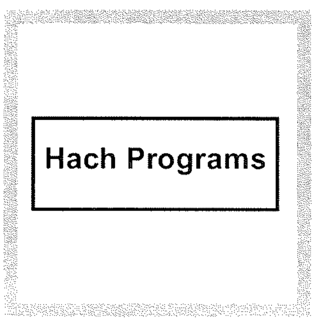
0.00 mg/L Fe



8. Place the prepared sample into the cell holder.

Results will appear in mg/L Fe.

AccuVac Ampul — Method 8008



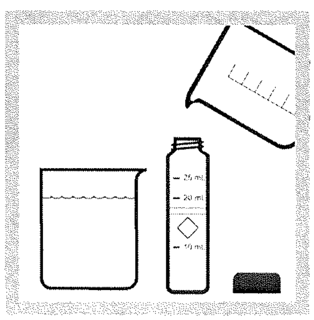
1. Touch

Hach Programs.

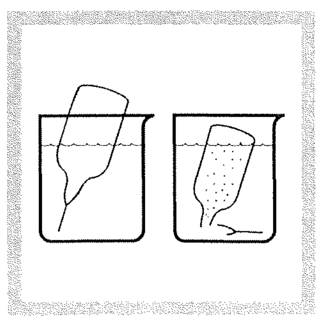
Select program

267 Iron, FerroVer AV.

Touch **Start**.

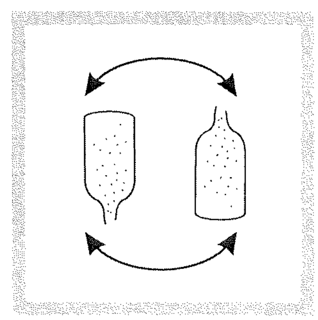


2. Fill a sample cell with 25 mL of sample. Collect at least 40 mL of sample in a 50-mL beaker.

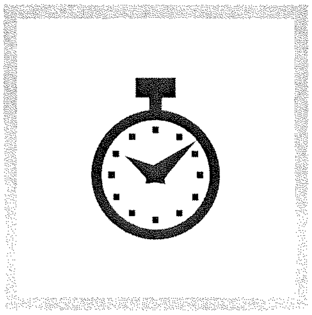


3. Fill a FerroVer Iron AccuVac® Ampul with sample.

Keep the tip immersed while the ampule fills completely.



4. Quickly invert the ampule several times to mix. Wipe off any liquid or fingerprints.

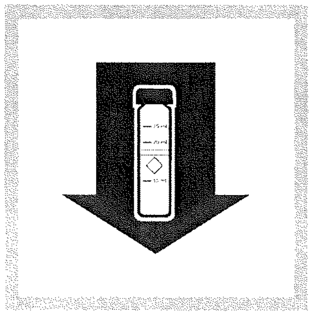


5. Touch the timer icon.

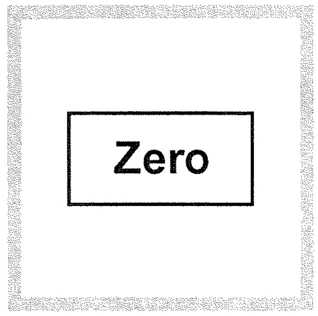
Touch **OK**.

A three-minute reaction period will begin.

(Samples that contain rust should react for at least 5 minutes.)



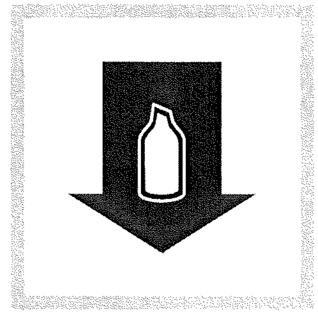
6. When the timer beeps, place the blank into the cell holder.



7. Touch **Zero**.

The display will show:

0.00 mg/L Fe



8. Place the AccuVac Ampul into the cell holder.

Results will appear in mg/L Fe.

Interferences

Interfering Substance	Interference Levels and Treatments
Calcium, Ca^{2+}	No effect at less than 10,000 mg/L as $CaCO_3$.
Chloride, Cl^-	No effect at less than 185,000 mg/L.
Copper, Cu^{2+}	No effect. Masking agent is contained in FerroVer Reagent.
High Iron Levels	Inhibit color development. Dilute sample and re-test to verify results.
Iron Oxide	Requires mild, vigorous or Digesdahl digestion. After digestion, adjust sample to pH 3–5 with sodium hydroxide (Cat. No. 2450-32), then analyze.
Magnesium	No effect at 100,000 mg/L as calcium carbonate.
Molybdate Molybdenum	No effect at 50 mg/L as Mo.
High Sulfide Levels, S^{2-}	**1.** Treat in fume hood or well-ventilated area. Add 5 mL hydrochloric acid, ACS (Cat. No. 134-49) to 100 mL sample in a 250-mL Erlenmeyer flask. Boil 20 minutes. **2.** Cool. Adjust pH to 3–5 with Sodium Hydroxide (Cat. No. 2450-32). Readjust volume to 100 mL with deionized water. **3.** Analyze.
Turbidity	**1.** Add 0.1 g scoop of RoVer® Rust Remover (Cat. No. 300-01) to the blank. Swirl to mix. **2.** Zero the instrument with this blank. **3.** If sample remains turbid, add three 0.2 g scoops of RoVer to a 75-mL sample. Let stand 5 minutes. **4.** Filter through a Glass Membrane Filter (Cat. No. 2530-00) and Filter Holder (Cat No. 2340-00). **5.** Use filtered sample in steps 2 and 5.
Extreme Sample pH	Adjust pH to 3–5. See *Section 3.3 Interferences* on page *50*.
Highly Buffered Samples	Adjust pH to 3–5. See *Section 3.3 Interferences* on page *50*.

Sample Collection, Storage and Preservation

Collect samples in acid-cleaned glass or plastic containers. No acid addition is necessary if analyzing the sample immediately. To preserve samples, adjust the pH to 2 or less with concentrated nitric acid (about 2 mL per liter) (Cat. No. 152-49). Preserved samples may be stored up to six months at room temperature. Before analysis, adjust the pH to between 3 and 5 with 5.0 N Sodium Hydroxide Standard Solution (Cat. No. 2450-32). Correct the test result for volume additions; see *Section 3.1.3 Correcting for Volume Additions* on page *43*.

If only dissolved iron is to be determined, filter the sample before acid addition.

Accuracy Check

Standard Additions Method (Sample Spike)

1. After reading test results, leave the sample cell (unspiked sample) in the instrument.
2. Touch **Options**. Touch **Standard Additions**. A summary of the standard additions procedure will appear.
3. Touch **OK** to accept the default values for standard concentration, sample volume, and spike volumes. Touch **Edit** to change these values. After values are accepted, the unspiked sample reading will appear in the top row. See *Standard Additions* in the instrument manual for more information.
4. Snap the neck off an Iron Voluette Ampule Standard, 50-mg/L.
5. Prepare a 0.1 mL sample spike by adding 0.1 mL of standard to the unspiked sample. Touch the timer icon. After the timer beeps, read the result.
6. Prepare a 0.2 mL sample spike by adding 0.1 mL of standard to the 0.1 mL sample spike. Touch the timer icon. After the timer beeps, read the result.
7. Prepare a 0.3 mL sample spike by adding 0.1 mL of standard to the 0.2 mL sample spike. Touch the timer icon. After the timer beeps, read the result. Each addition should reflect approximately 100% recovery.

Note: *For AccuVac Ampuls, fill three mixing cylinders (Cat. No. 1896-41) with 50-mL of sample and spike with 0.2 mL, 0.4 mL, and 0.6 mL of standard. Transfer 40 mL from each of the three mixing cylinders to three 50-mL beakers (Cat. No. 500-41H). Analyze each standard addition sample as described in the procedure above. Accept each standard additions reading by touching* **Read**. *Each addition should reflect approximately 100% recovery.*

8. After completing the sequence, touch **Graph** to view the best-fit line through the standard additions data points, accounting for matrix interferences. Touch **View: Fit**, then select **Ideal Line** and touch **OK** to view the relationship between the sample spikes and the "Ideal Line" of 100% recovery.

See *Section 3.2.2 Standard Additions* on page *46* for more information.

Standard Solution Method

1. Prepare a 1.00-mg/L Fe standard solution by pipetting 1.00 mL of Iron Standard Solution, 100-mg/L, into a 100-mL volumetric flask. Dilute to the mark with deionized water. Stopper and invert to mix. Prepare this solution daily. Perform the iron procedure as described above.
2. To adjust the calibration curve using the reading obtained with the 1.00 mg/L Standard Solution, touch **Options** on the current program menu. Touch **Standard Adjust**.

3. Touch **On**. Touch **Adjust** to accept the displayed concentration. If an alternate concentration is used, touch the number in the box to enter the actual concentration, then touch **OK**. Touch **Adjust**.

See *Section 3.2.4 Adjusting the Standard Curve* on page *49* for more information.

Method Performance

Precision

Standard: 1.000 mg/L Fe

Program	95% Confidence Limits of Distribution
265	0.989–1.011 mg/L Fe
267	0.977–1.023 mg/L Fe

See *Section 3.4.3 Precision* on page *53* for more information, or if the standard concentration did not fall within the specified range.

Sensitivity

Program	Portion of Curve	ΔAbs	ΔConcentration
265	Entire range	0.010	0.022 mg/L Fe
267	Entire range	0.010	0.023 mg/L Fe

See *Section 3.4.5 Sensitivity* on page *54* for more information.

Summary of Method

FerroVer Iron Reagent converts all soluble iron and most insoluble forms of iron in the sample to soluble ferrous iron. The ferrous iron reacts with the 1,10 phenanthroline indicator in the reagent to form an orange color in proportion to the iron concentration. Test results are measured at 510 nm.

Required Reagents

Description	Quantity Required per test	Unit	Cat. No.
FerroVer® Iron Reagent Powder Pillows (for 10-mL sample)	1 pillow	100/pkg	21057-69
or			
FerroVer® Iron Reagent AccuVac® Ampuls	1 ampul	25/pkg	25070-25

Required Apparatus

Description	Quantity Required per test	Unit	Cat. No.
Sample Cells, 10-mL, w/cap	2	6/pkg	24276-06
Beaker, 50-mL	1	each	500-41H

Required Standards

Description	Unit	Cat. No.
Iron Standard Solution, 100-mg/L	100 mL	14175-42
Iron Standard Solution, 10-mL Voluette® Ampule, 50-mg/L as Fe	16/pkg	14254-10
Water, deionized	4 liters	272-56

Iron, Ferrous

Method 8146 | **1, 10 Phenanthroline Method***

Powder Pillows or AccuVac® Ampuls | **(0.02 to 3.00 mg/L)**

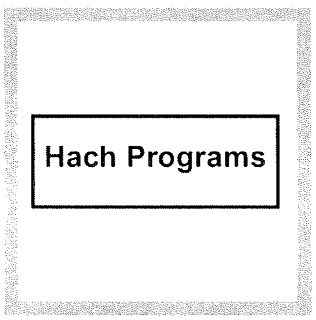
Scope and Application: For water, wastewater, and seawater

* Adapted from *Standard Methods for the Examination of Water and Wastewater*, 15th ed. 201 (1980)

Tips and Techniques

- Analyze samples as soon as possible to prevent air oxidation of ferrous iron to ferric iron, which is not determined.
- For more accurate results, determine a reagent blank value for each new lot of reagent. Follow the procedure using deionized water in place of the sample. Subtract the reagent blank value from the final results or perform a reagent blank adjust. See the instrument manual for more information on *Running a Reagent Blank*.
- If ferrous iron is present, an orange color will form after adding the reagent.

Powder Pillows — Method 8146



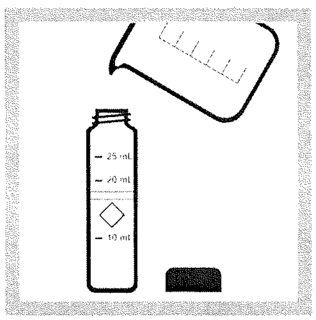
1. Touch

Hach Programs.

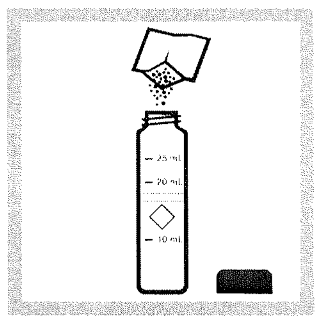
Select program

255 Iron, Ferrous.

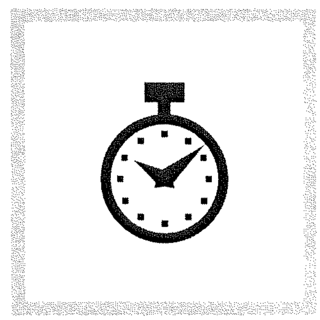
Touch **Start**.



2. Fill a clean, round sample cell with 25 mL of sample.



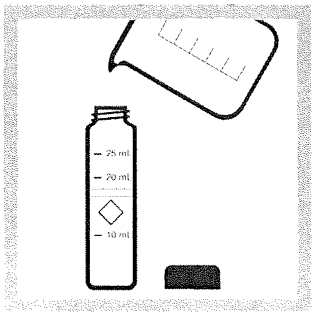
3. Add the contents of one Ferrous Iron Reagent Powder Pillow to the sample cell (the prepared sample). Swirl to mix.



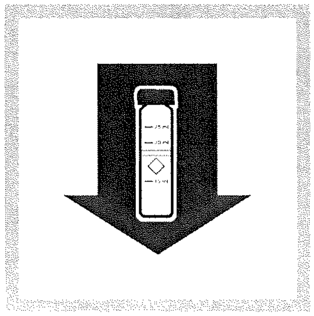
4. Touch the timer icon.

Touch **OK**.

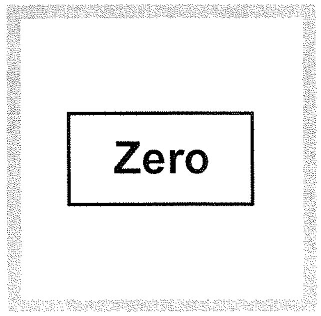
A three-minute reaction period will begin.



5. Fill a second round sample cell with 25 mL of sample (the blank).



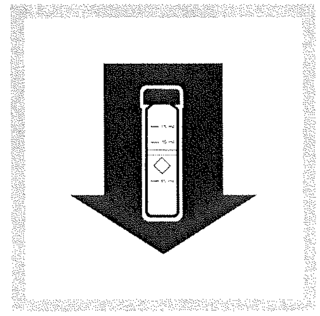
6. When the timer beeps, place the blank into the cell holder.



7. Touch **Zero**.

The display will show:

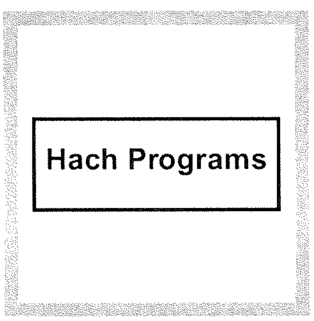
0.00 mg/L Fe^{2+}



8. Place the prepared sample into the cell holder.

Results will appear in mg/L Fe^{2+}.

AccuVac Ampul — Method 8146



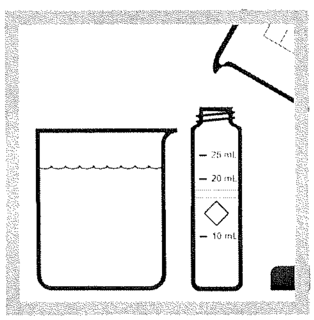
1. Touch

Hach Programs.

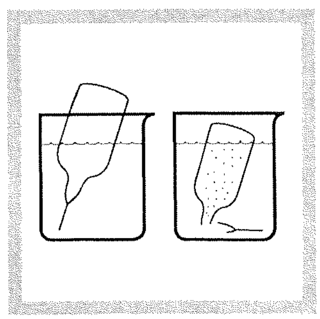
Select program

257 Iron, Ferrous AV.

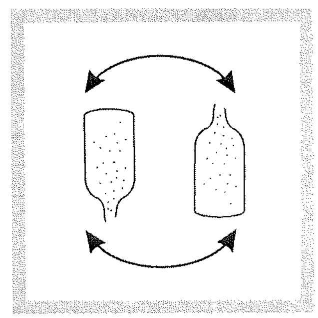
Touch **Start**.



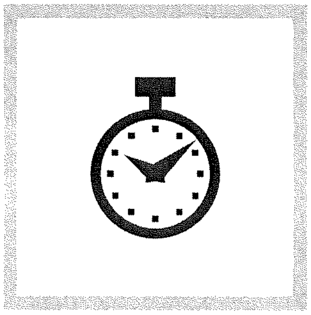
2. Fill a sample cell with 25 mL of sample (the blank). Collect at least 40 mL of sample in a 50-mL beaker.



3. Fill a Ferrous Iron AccuVac® Ampul with sample. Keep the tip immersed while the ampule fills completely.



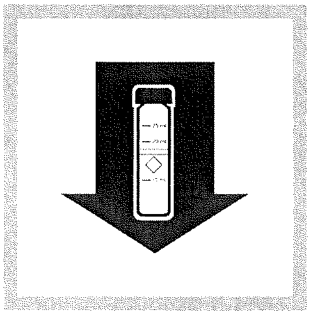
4. Quickly invert the ampule several times to mix. Wipe off any liquid or fingerprints.



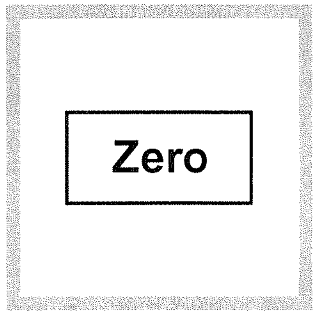
5. Touch the timer icon.

Touch **OK**.

A three-minute reaction period will begin.



6. When the timer beeps, place the blank into the cell holder.



7. Touch **Zero**.

The display will show:

0.00 mg/L Fe^{2+}

8. Place the AccuVac Ampul into the cell holder.

Results will appear in mg/L Fe^{2+}.

Sample Collection, Storage and Preservation

Collect samples in plastic or glass bottles. Analyze samples as soon as possible after collection.

Accuracy Check

Standard Solution Method

1. Prepare a ferrous iron stock solution (100-mg/L Fe^{2+}) by dissolving 0.7022 grams of Ferrous Ammonium Sulfate, hexahydrate, in deionized water. Dilute to one liter in a Class A volumetric flask. In a 100-mL Class A volumetric flask, dilute 1.00 mL of this solution to 100 mL with deionized water to make a 1.0-mg/L standard solution. Prepare this solution immediately before use. Perform the iron procedure as described above.
2. To adjust the calibration curve using the reading obtained with the 1.0-mg/L Fe^{2+} Standard Solution, touch **Options** on the current program menu. Touch **Standard Adjust**.
3. Touch **On**. Touch **Adjust** to accept the displayed concentration. If an alternate concentration is used, touch the number in the box to enter the actual concentration, then touch **OK**. Touch **Adjust**.

See *Section 3.2.4 Adjusting the Standard Curve* on page *49* for more information.

Method Performance

Precision

Standard: 1.000 mg/L Fe

Program	95% Confidence Limits of Distribution
255	0.989–1.011 mg/L Fe
257	0.977–1.023 mg/L Fe

See *Section 3.4.3 Precision* on page *53* for more information, or if the standard concentration did not fall within the specified range.

Sensitivity

Program	Portion of Curve	ΔAbs	ΔConcentration
255	Entire range	0.010	mg/L Fe
257	Entire range	0.010	0.023 mg/L Fe

See *Section 3.4.5 Sensitivity* on page *54* for more information.

Summary of Method

The 1,10 phenanthroline indicator in the Ferrous Iron Reagent reacts with ferrous iron in the sample to form an orange color in proportion to the iron concentration. Ferric iron does not react. The ferric iron (Fe^{3+}) concentration can be determined by subtracting the ferrous iron concentration from the results of a total iron test. Test results are measured at 510 nm.

Required Reagents

Description	Quantity Required per test	Unit	Cat. No.
Ferrous Iron Reagent AccuVac® Ampuls	1 ampul	25/pkg	25140-25
or			
Ferrous Iron Reagent Powder Pillows	1 pillow	100/pkg	1037-69

Required Apparatus

Description	Quantity Required per test	Unit	Cat. No.
Beaker, 50-mL	1	each	500-41H
Sample Cells, 10-20-25 mL, w/cap	2	6/pkg	24019-06

Required Standards

Description	Quantity Required per test	Unit	Cat. No.
Ferrous Ammonium Sulfate, hexahydrate, ACS		113 g	11256-14
Water, deionized		4 liters	272-56

Sulfate

✔Method 8051 — SulfaVer 4 Method*

Powder Pillows or AccuVac® Ampuls (2 to 70 mg/L)

Scope and Application: For water, wastewater, and seawater; USEPA accepted for reporting wastewater analyses

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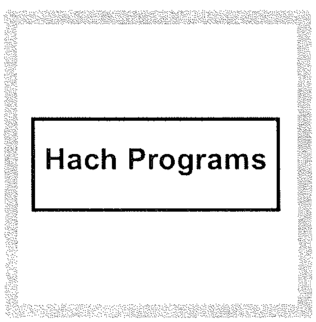
* Adapted from *Standard Methods for the Examination of Water and Wastewater.* Procedure is equivalent to USEPA method 375.4 for wastewater.

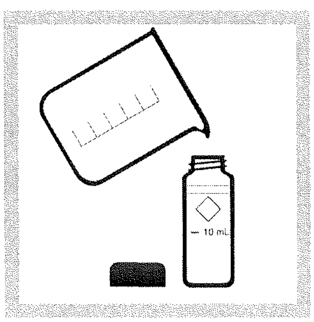
Tips and Techniques

- You must adjust the standard curve for each new lot of reagent. See *Standard Solutions* following these steps.
- For best results, perform a new calibration for each lot of reagent. See *Calibration Standard Preparation* following these steps.
- For more accurate results, determine a reagent blank value for each new lot of reagent. Follow the procedure using deionized water in place of the sample. Subtract the reagent blank value from the final results or perform a reagent blank adjust. See the instrument manual for more information on *Running a Reagent Blank*.
- Filter highly colored or turbid samples using filter paper (Cat. No. 1894-57) and a funnel (Cat. No. 1083-67). Use this sample in *step 5*.
- After adding reagent to the sample, a white turbidity will form if sulfate is present.
- Undissolved powder that has settled does not affect accuracy.
- SulfaVer® 4 contains barium chloride. The final solution will contain barium chloride (D005) at a concentration regulated as a hazardous waste by the Federal RCRA. See *Section 5* for more information on proper disposal of these materials.

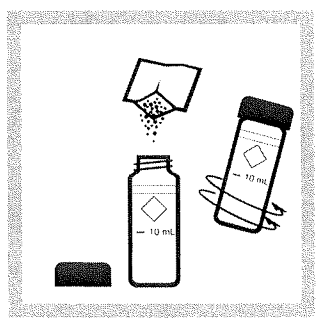
Powder Pillows — Method 8051



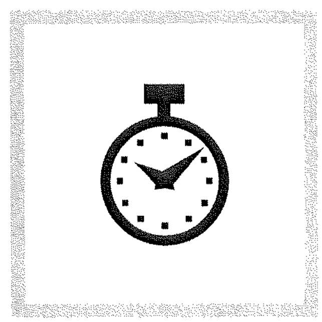
1. Touch **Hach Programs**. Select program **680 Sulfate**. Touch **Start**.



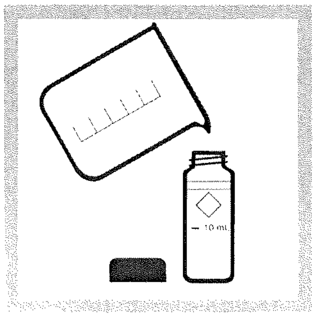
2. Fill a clean sample cell with 10 mL of sample.



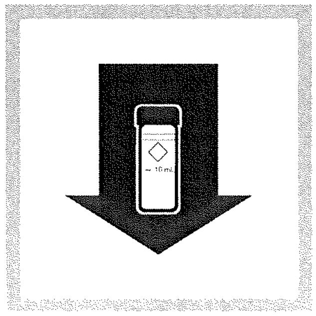
3. Add the contents of one SulfaVer 4 Reagent Powder Pillow to the sample cell (the prepared sample). Swirl to mix.



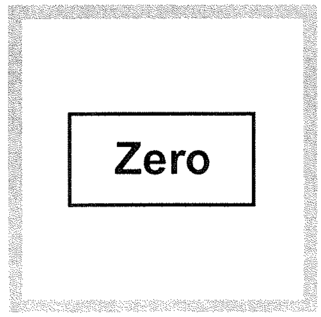
4. Touch the timer icon. Touch **OK**. A five-minute reaction period will begin. Do not disturb the cell during this time.



5. Fill a second sample cell with 10 mL of sample (the blank).



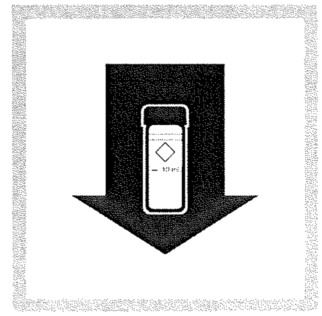
6. When the timer beeps, place the blank into the cell holder.



7. Touch **Zero**.

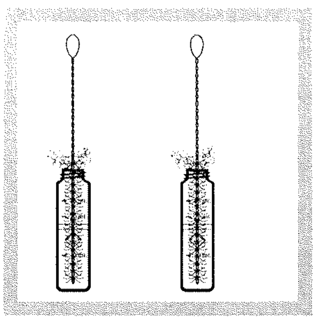
The display will show:

0 mg/L SO_4^{2-}



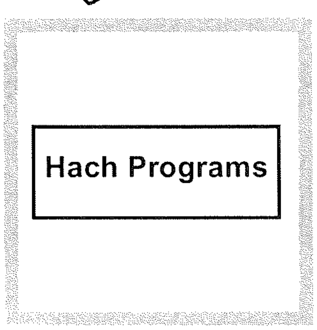
8. Within five minutes after the timer beeps, place the prepared sample into the cell holder.

Results will appear in mg/L SO_4^{2-}.



9. Clean the sample cells with soap and a brush.

AccuVac Ampul — Method 8051



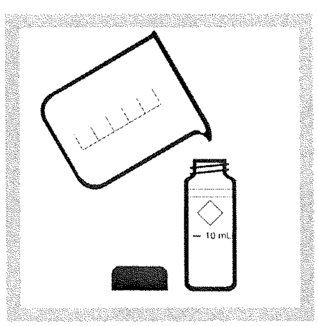
1. Touch

Hach Programs.

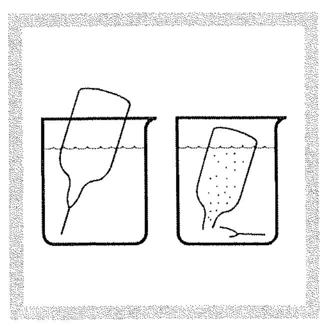
Select program

685 Sulfate AV.

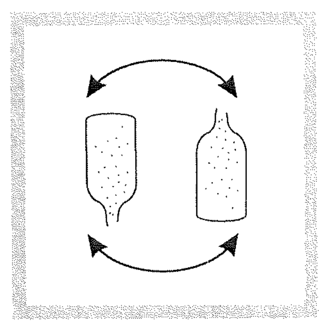
Touch **Start**.



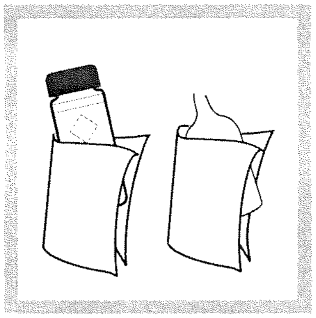
2. Fill a clean sample cell with 10 mL of sample (the blank). Collect at least 40 mL of sample in a 50-mL beaker.



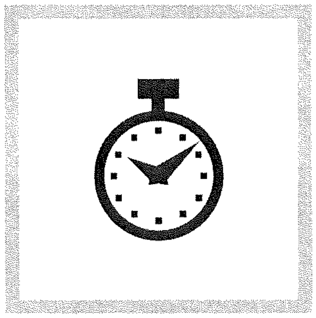
3. Fill a SulfaVer 4 Sulfate AccuVac Ampul with sample. Keep the tip immersed until the ampule fills completely.



4. Quickly invert the ampule several times to mix.



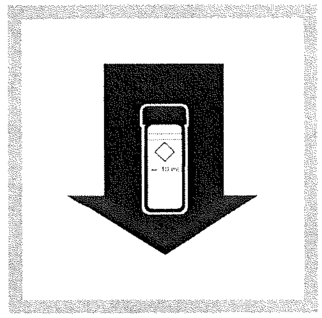
5. Wipe off any liquid or fingerprints from the blank and the ampule.



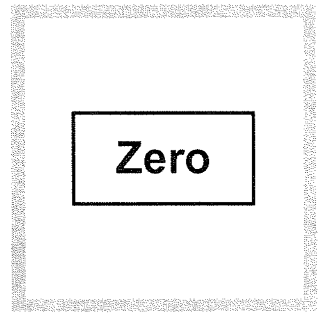
6. Touch the timer icon.

Touch **OK**.

A five-minute reaction period will begin. Do not disturb the cell during this time.



7. When the timer beeps, place the blank into the cell holder.



8. Touch **Zero**.

The display will show:

0 mg/L SO_4^{2-}

9. Within five minutes after the timer beeps, place the ampule into the cell holder.

Results will appear in mg/L SO_4^{2-}.

Interferences

Interfering Substance	Interference Levels and Treatments
Calcium	Greater than 20,000 mg/L as $CaCO_3$
Chloride	Greater than 40,000 mg/L as Cl
Magnesium	Greater than 10,000 mg/L as $CaCO_3$
Silica	Greater than 500 mg/L as SiO_2

Sample Collection, Storage, and Preservation

Collect samples in clean plastic or glass bottles. Samples may be stored up to 7 days by cooling to 4 °C (39 °F) or lower. Warm to room temperature before analysis.

Accuracy Check

Standard Additions Method (Sample Spike)

1. After reading test results, leave the sample cell (unspiked sample) in the instrument.
2. Touch **Options**. Touch **Standard Additions**. A summary of the standard additions procedure will appear.
3. Touch **OK** to accept the default values for standard concentration, sample volume, and spike volumes. Touch **Edit** to change these values. After values are accepted, the unspiked sample reading will appear in the top row. See *Standard Additions* in the instrument manual for more information.
4. Snap the neck off a Sulfate 2-mL Ampule Standard, 1000-mg/L sulfate.
5. Prepare three sample spikes. Fill three mixing cylinders (Cat. No. 1896-40) with 25 mL of sample. Use the TenSette Pipet to add 0.1 mL, 0.2 mL, and 0.3 mL of standard, respectively, to each sample and mix thoroughly.
6. Transfer 10 mL of each sample spike to a clean sample cell and analyze each sample spike as described in the procedure above, starting with the 0.1 mL sample spike. Accept each standard additions reading by touching **Read**. Each addition should reflect approximately 100% recovery.

Note: *For AccuVac Ampuls, fill three Mixing Cylinders (Cat. No. 1896-41) with 50 mL of sample and spike with 0.2 mL, 0.4 mL, and 0.6 mL of standard. Transfer 40 mL from each of the three mixing cylinders to three 50-mL Beakers (Cat. No. 500-41). Analyze each standard addition sample as described in the procedure above. Accept each standard additions reading by touching* **Read**. *Each addition should reflect approximately 100% recovery.*

7. After completing the sequence, touch **Graph** to view the best-fit line through the standard additions data points, accounting for matrix interferences. Touch **View: Fit**, then select **Ideal Line** and touch **OK** to view the relationship between the sample spikes and the "Ideal Line" of 100% recovery.

See *Section 3.2.2 Standard Additions* on page *46* for more information.

Standard Solutions

Prepare a 70-mg/L sulfate standard solution as follows:

1. Using Class A glassware, Pipet 7 mL of Sulfate Standard Solution, 1000-mg/L, into a 100-mL volumetric flask. Dilute to the mark with deionized water. Prepare this solution daily. Perform the SulfaVer procedure as described above.
2. To adjust the calibration curve using the reading obtained with the 70-mg/L standard solution, touch **Options** on the current program menu. Touch **Standard Adjust**.
3. Touch **On**. Touch **OK** to accept the displayed concentration. If an alternate concentration is used, touch **Adjust** and then enter the actual concentration. Touch **OK**.

See *Section 3.2.4 Adjusting the Standard Curve* on page *49* for more information.

Calibration Standard Preparation

To perform a sulfate calibration using the SulfaVer method, use Class A glassware to prepare calibration standards containing 10, 20, 30, 40, 50, 60 and 70 mg/L SO_4^{2-} as follows:

1. Into seven different 100-mL Class A volumetric flasks, pipet 1, 2, 3, 4, 5, 6, and 7 mL of the 1000-mg/L Sulfate Standard Solution.
2. Dilute to the mark with deionized water. Mix thoroughly.
3. Using the SulfaVer method and the calibration procedure described in the User-Entered Programs section of the spectrophotometer *Instrument Manual*, generate a calibration curve from the calibration standards prepared above.

Method Performance

Precision

Standard: 30 mg/L SO_4^{2-}

Program	95% Confidence Limits of Distribution
680	27–33 mg/L SO_4^{2-}
685	18–43 mg/L SO_4^{2-}

See *Section 3.4.3 Precision* on page *53* for more information, or if the standard concentration did not fall within the specified range.

Sensitivity

Program	ΔAbs	ΔConcentration
680	0.010	1 mg/L SO_4^{2-}
685	0.010	2 mg/L SO_4^{2-}

See *Section 3.4.5 Sensitivity* on page *54* for more information.

Summary of Method

Sulfate ions in the sample react with barium in the SulfaVer 4 and form a precipitate of barium sulfate. The amount of turbidity formed is proportional to the sulfate concentration. The SulfaVer 4 also contains a stabilizing agent to hold the precipitate in suspension. Test results are measured at 450 nm.

Required Reagents

Description	Quantity Required per test	Unit	Cat. No.
SulfaVer® 4 Reagent Powder Pillows	1	100/pkg	21067-69
or			
SulfaVer® 4 Sulfate Reagent AccuVac Ampuls	1	25/pkg	25090-25

Required Apparatus

Description	Quantity Required per test	Unit	Cat. No.
Beaker, 50-mL	1	each	500-41
Sample cells, 10-mL, w/cap	2	6/pkg	24276-06

Required Standards

Description	Quantity Required per test	Unit	Cat. No.
Sulfate Standard Solution, 1000-mg/L		500 mL	21757-49
Sulfate Standard Solution, 1000-mg/L, 2-mL Ampules		20/pkg	21757-20
Water, deionized		4 liters	272-56

Nitrate

Method 10020 — Chromotropic Acid Method

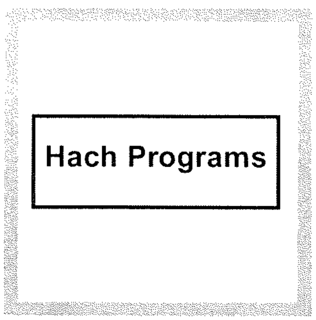
Test 'N Tube™ Vials — **HR (0.2 to 30.0 mg/L NO_3^-–N)**

Scope and Application: For water and wastewater

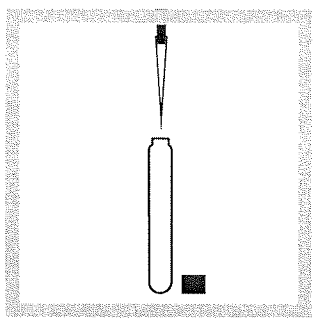
Tips and Techniques

- For more accurate results, determine a reagent blank value for each new lot of reagent. Follow the procedure using deionized water (nitrate-free) in place of the sample. Subtract the reagent blank value from the final results or perform a reagent blank adjust. See the instrument manual for more information on *Running a Reagent Blank*.
- This test is technique-sensitive. Invert the vials as described here to avoid low results: Hold the vial in a vertical position with the cap pointing up. Turn the vial upside-down. Wait for all of the solution to flow down to the cap. Pause. Return the vial to an upright position. Wait for all the solution to flow to the bottom of the vial. This process equals one inversion.
- Wipe the outside of sample cells before each insertion into the instrument cell holder. Use a damp towel followed by a dry one to remove fingerprints or other marks.

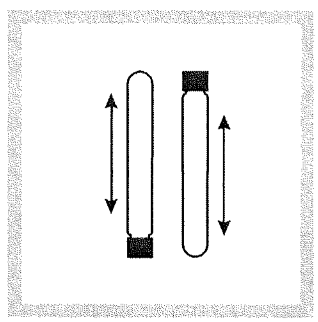
Test 'N Tube — Method 10020



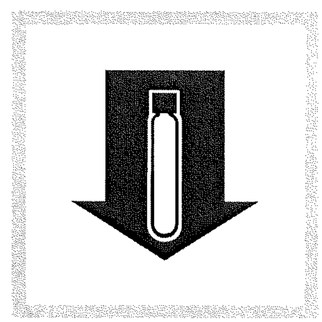
1. Touch **Hach Programs**. Select program **344 N, Nitrate HR TNT**. Touch **Start**.



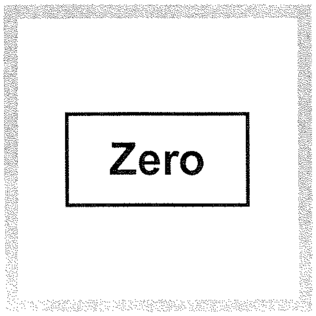
2. Remove the cap from a NitraVer X Reagent A Test 'N Tube vial and add 1.00 mL of sample (this is the blank).



3. Cap the tube and invert ten times to mix.



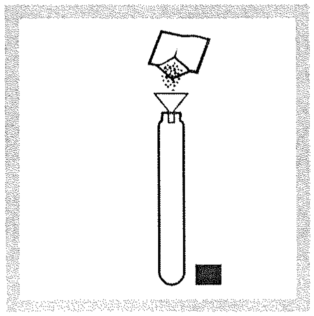
4. Wipe the blank and place it into the cell holder.



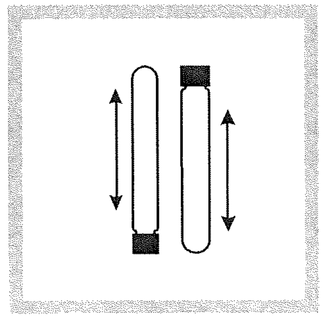
5. Touch **Zero**.

The display will show:

0.0 mg/L NO_3^-–N

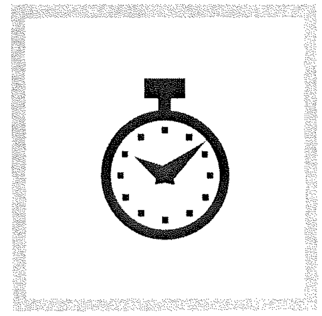


6. Remove the vial from the instrument. Using a funnel, add the contents of one NitraVer X Reagent B Powder Pillow to the vial.



7. Cap and invert ten times to mix (this is the *prepared sample*).

Some solid matter will not dissolve.

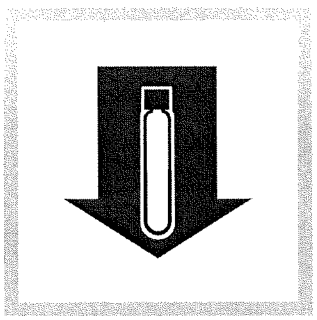


8. Touch the timer icon.

Touch **OK**.

A five-minute reaction period will begin. Do not invert the vial again.

A yellow color will develop if nitrate is present.



9. **Within five minutes** after the timer beeps, wipe the prepared sample and place it into the cell holder. Results will appear in mg/L NO_3^-–N.

Interferences

Interfering Substance	Interference Levels and Treatments
Barium	A negative interference at concentrations greater than 1 mg/L.
Chloride	Does not interfere below 1000 mg/L.
Nitrite	A positive interference at concentrations greater than 12 mg/L. Remove nitrite interference up to 100 mg/L by adding 400 mg (one full 0.5 g Hach measuring spoon) of Urea (Cat. No. 11237-26) to 10 mL of sample. Swirl to dissolve. Proceed with the nitrate test as usual.
Copper	Positive at all levels.

Sample Collection, Preservation, and Storage

Collect samples in clean plastic or glass bottles. Store at 4 °C (39 °F) or lower if the sample is to be analyzed within 24 to 48 hours. Warm to room temperature before running the test. For longer storage periods (up to 14 days), adjust sample pH to 2 or less with Concentrated Sulfuric Acid, ACS (about 2 mL per liter) (Cat. No. 979-49). Sample refrigeration is still required.

Before testing the stored sample, warm to room temperature and neutralize with 5.0 N Sodium Hydroxide Standard Solution (Cat. No. 2450-26).

Do not use mercury compounds as preservatives.

Correct the test result for volume additions; see *Section 3.1.3 Correcting for Volume Additions* on page *43*.

Accuracy Check

Standard Additions Method (Sample Spike)

1. After reading test results, leave the sample cell (unspiked sample) in the instrument. Verify the chemical form.
2. Touch **Options**. Touch **Standard Additions**. A summary of the standard additions procedure will appear.
3. Touch **OK** to accept the default values for standard concentration, sample volume, and spike volumes. Touch **Edit** to change these values. After values are accepted, the unspiked sample reading will appear in the top row. See *Standard Additions* in the instrument manual for more information.
4. Snap the neck off a High Range Nitrate Nitrogen Voluette® Ampule Standard, 500 mg/L NO_3^-–N.
5. Prepare three sample spikes. Fill three mixing cylinders (Cat. No. 1896-40) with 25 mL of sample. Use the TenSette® Pipet to add 0.1 mL, 0.2 mL, and 0.3 mL of standard, respectively, to each sample and mix thoroughly.
6. Analyze each sample spike as described in the procedure above, starting with the 0.1 mL sample spike. Accept each standard additions reading by touching **Read**. Each addition should reflect approximately 100% recovery.
7. After completing the sequence, touch **Graph** to view the best-fit line through the standard additions data points, accounting for matrix interferences. Touch **View: Fit**, then select **Ideal Line** and touch **OK** to view the relationship between the sample spikes and the "Ideal Line" of 100% recovery.

See *Section 3.2.2 Standard Additions* on page *46* for more information.

Standard Solution Method

Use a 10.0-mg/L Nitrate Nitrogen Standard Solution to check test accuracy.

See *Section 3.2.1 Standard Solutions* on page *45* for more information.

Method Performance

Precision

Standard: 10.0 mg/L NO_3^-–N

Program	95% Confidence Limits of Distribution
344	9.5–10.5 mg/L NO_3^-–N

See *Section 3.4.3 Precision* on page *53* for more information, or if the standard concentration did not fall within the specified range.

Sensitivity

Portion of Curve	ΔAbs	ΔConcentration
Entire range	0.010	0.2 mg/L NO_3^-–N

See *Section 3.4.5 Sensitivity* on page *54* for more information.

Summary of Method

Nitrate in the sample reacts with chromotropic acid under strongly acidic conditions to yield a yellow product with a maximum absorbance at 410 nm.

Required Reagents

Description	Quantity Required Per Test	Unit	Cat. No.
Test 'N Tube NitraVer® X Nitrate Reagent Set (50 tests)			26053-45

Required Apparatus

Description	Quantity Required Per Test	Unit	Cat. No.
Funnel, micro, poly	1	each	25843-35
Pipet, TenSette®, 0.1 to 1.0 mL	1	each	19700-01
Pipet Tips, for 19700-01 TenSette® Pipet	varies	50/pkg	21856-96
Sample Cells, 10-mL, w/cap	2	6/pkg	24276-06
Test Tube Rack, cooling	1–3	each	18641-00

Required Standards

Description	Quantity Required Per Test	Unit	Cat. No.
Nitrate Nitrogen Standard Solution, 10-mg/L N		500 mL	307-49
Nitrate Nitrogen Standard Solution, Voluette® Ampule, 500-mg/L N		16/pkg	14260-10
Water, deionized		4 liters	272-56

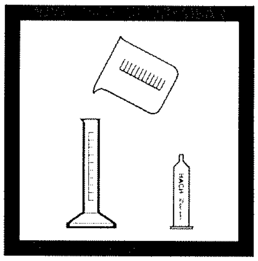
FOR TECHNICAL ASSISTANCE, PRICE INFORMATION AND ORDERING:
In the U.S.A. – Call toll-free 800-227-4224
Outside the U.S.A. – Contact the HACH office or distributor serving you.
On the Worldwide Web – www.hach.com; E-mail – techhelp@hach.com

HACH COMPANY
WORLD HEADQUARTERS
Telephone: (970) 669-3050
FAX: (970) 669-2932

Method 8203

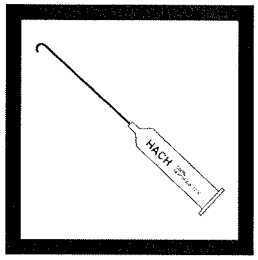
ALKALINITY (10 to 4000 mg/L as $CaCO_3$)

Phenolphthalein and Total Method

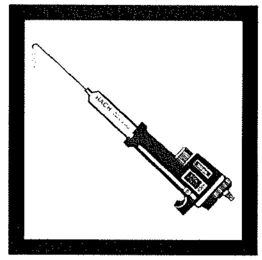


1. Select the sample volume and Sulfuric Acid (H_2SO_4) Titration Cartridge corresponding to the expected alkalinity concentration as mg/L calcium carbonate ($CaCO_3$) from *Table 1*.

Note: *See Sampling and Storage following these steps.*

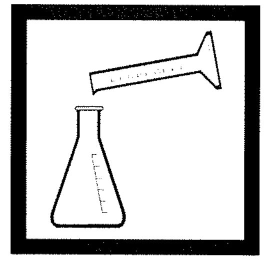


2. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step* for assembly instructions, if necessary.



3. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

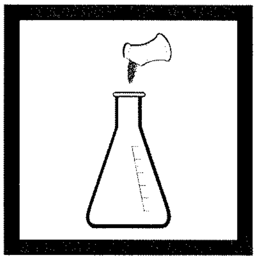
Note: *For added convenience use the TitraStir® Stir Plate. See General Description, Step 3 in Step-by-Step.*



4. Use a graduated cylinder or pipet to measure the sample volume from *Table 1*. Transfer the sample into a clean 250-mL Erlenmeyer flask. Dilute to about the 100-mL mark with deionized water, if necessary.

Table 1

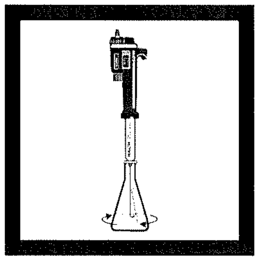
Range (mg/L as $CaCO_3$)	Sample Volume (mL)	Titration Cartridge (H_2SO_4)	Catalog Number	Digit Multiplier
10-40	100	0.1600	14388-01	0.1
40-160	25	0.1600	14388-01	0.4
100-400	100	1.600	14389-01	1.0
200-800	50	1.600	14389-01	2.0
500-2000	20	1.600	14389-01	5.0
1000-4000	10	1.600	14389-01	10.0



5. Add the contents of one Phenolphthalein Indicator Powder Pillow and swirl to mix.

Note: *A solution of one pH 8.3 Buffer Powder Pillow and one Phenolphthalein Powder Pillow in 50 mL of deionized water is recommended as a comparison for determining the proper end point color.*

Note: *Four drops of Phenolphthalein Indicator Solution may be substituted for the Phenolphthalein Indicator Powder Pillow.*



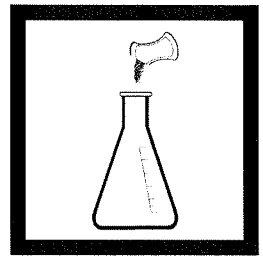
6. If the solution turns pink, titrate to a colorless end point. Place the delivery tube tip into the solution and swirl the flask while titrating with sulfuric acid. Record the number of digits required.

Note: *If the solution is colorless before titrating with sulfuric acid, the Phenolphthalein (P) Alkalinity is zero; proceed with step 8.*

Digits Required x Digit Multiplier = mg/L as $CaCO_3$ P Alkalinity

7. Calculate:

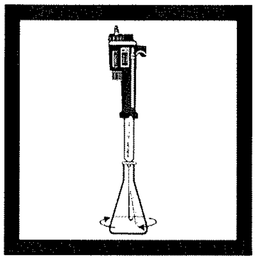
Digits Required x Digit Multiplier = mg/L $CaCO_3$ P Alkalinity

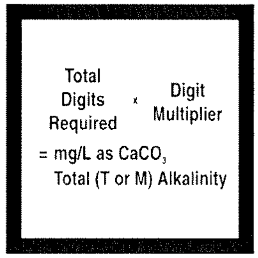


8. Add the contents of one Bromcresol Green-Methyl Red Indicator Powder Pillow to the flask and swirl to mix.

Note: *Four drops of Methyl Purple Indicator Solution may be substituted for the Bromcresol Green-Methyl Red Indicator Powder Pillow. Titrate from green to a gray end point (pH 5.1).*

Note: *Four drops of Bromcresol Green-Methyl Red Indicator Solution may be substituted for the Bromcresol Green-Methyl Red Indicator Powder Pillow.*





9. Continue the titration with sulfuric acid to a light greenish blue-gray (pH 5.1), a light violet-gray (pH 4.8), or a light pink (pH 4.5) color, as required by the sample composition; see *Table 2*. Record the number of digits required.

Note: *A solution of one Bromcresol Green-Methyl Red Powder Pillow and one pillow of the appropriate pH buffer in 50 mL of deionized water is recommended as a comparison for judging the proper end point color. If the pH 3.7 end point is used, use a Bromphenol Blue Powder Pillow instead of a Bromcresol Green-Methyl Red and titrate to a green end point.*

10. Calculate:

Total Digits Required x Digit Multiplier = mg/L as CaCO3 Total (T or M) Alkalinity

Note: *Carbonate, bicarbonate and hydroxide concentrations may be expressed individually using the relationships shown in Table 3.*

Note: *meq/L Alkalinity = mg/L as $CaCO_3$ ÷ 50.*

Table 2

Sample Composition	End Point
Alkalinity about 30 mg/L	pH 4.9
Alkalinity about 150 mg/L	pH 4.6
Alkalinity about 500 mg/L	pH 4.3
Silicates or Phosphates present	pH 4.5
Industrial waste or complex system	pH 4.5

Sampling and Storage

Collect samples in clean plastic or glass bottles. Fill completely and cap tightly. Avoid excessive agitation or prolonged exposure to air. Samples should be analyzed as soon as possible after collection but can be stored at least 24 hours by cooling to 4 °C (39 °F) or below. Warm to room temperature before analyzing.

Alkalinity Relationship Table

Total alkalinity primarily includes hydroxide, carbonate and bicarbonate alkalinities. The concentration of these alkalinities in a sample may be determined when the phenolphthalein and total alkalinities are known (see *Table 3*).

Table 3 Alkalinity Relationship

Row	Result of Titration	Hydroxide Alkalinity is equal to:	Carbonate Alkalinity is equal to:	Bicarbonate Alkalinity is equal to:
1	Phenolphthalein Alkalinity = 0	0	0	Total Alkalinity
2	Phenolphthalein Alkalinity equal to Total Alkalinity	Total Alkalinity	0	0
3	Phenolphthalein Alkalinity less than one half of Total Alkalinity	0	2 times the Phenolphthalein Alkalinity	Total Alkalinity minus two times Phenolphthalein Alkalinity
4	Phenolphthalein Alkalinity equal to one half of Total Alkalinity	0	Total Alkalinity	0
5	Phenolphthalein Alkalinity greater than one half of Total Alkalinity	2 times the Phenolphthalein minus Total Alkalinity	2 times the difference between Total and Phenolphthalein Alkalinity	0

To use the table follow these steps:

a. Does the phenolphthalein alkalinity equal zero? If yes, use Row 1.

b. Does the phenolphthalein alkalinity equal total alkalinity? If yes, use Row 2.

c. Multiply the phenolphthalein alkalinity by 2.

d. Select Row 3, 4, or 5 based on comparing the result of *step c* with the total alkalinity.

e. Perform the required calculations in the appropriate row, if any.

f. Check your results. The sum of the three alkalinity types will equal the total alkalinity.

For example:
A sample has 170 mg/L as $CaCO_3$ phenolphthalein alkalinity and 250 mg/L as $CaCO_3$ total alkalinity. What is the concentration of hydroxide, carbonate and bicarbonate alkalinities?

The phenolphthalein alkalinity does not equal 0 (it is 170 mg/L), see *step a*.

The phenolphthalein alkalinity does not equal total alkalinity (170 mg/L vs. 250 mg/L), see *step b*.

The phenolphthalein alkalinity multiplied by 2 = 340 mg/L, see *step c*.

Because 340 mg/L is greater than 250 mg/L, select Row 5, see *step d*.

The hydroxide alkalinity is equal to: (see *step e*).

340 – 250 = 90 mg/L hydroxide alkalinity

The carbonate alkalinity is equal to:

250 – 170 = 80
80 x 2 = 160 mg/L carbonate alkalinity

The bicarbonate alkalinity equals 0 mg/L.

Check: (see *step f*).

90 mg/L hydroxide alkalinity + 160 mg/L carbonate alkalinity +
0 mg/L bicarbonate alkalinity = 250 mg/L

The above answer is correct; the sum of each type equals the total alkalinity.

Accuracy Check

Standard Additions Method

This accuracy check should be performed when interferences are suspected or to verify analytical technique.

1. Snap the neck off an Alkalinity Standard Solution Voluette® Ampule, 0.500 N.
2. Use a TenSette® Pipet to add 0.1 mL of standard to the sample titrated in Steps 6 or 9. Resume titration back to the same end point. Record the number of digits needed.
3. Repeat, using two more additions of 0.1 mL. Titrate to the end point after each addition.
4. Each 0.1 mL addition of standard should require 25 additional digits of 1.600 N titrant or 250 digits of 0.1600 N titrant. If these uniform increases do not occur, refer to *Appendix A, Accuracy Check and Standard Additions*.

Interferences

- Highly colored or turbid samples may mask the color change at the end point. Use a pH meter for these samples.
- Chlorine may interfere with the indicators. Add one drop of 0.1 N Sodium Thiosulfate to eliminate this interference.

Summary of Method

The sample is titrated with sulfuric acid to a colorimetric end point corresponding to a specific pH. Phenolphthalein alkalinity is determined by titration to a pH of 8.3, as evidenced by the color change of phenolphthalein indicator, and indicates the total hydroxide and one half the carbonate present. M (methyl orange) or T (total) alkalinity is determined by titration to a pH between 3.7 and 5.1, and includes all carbonate, bicarbonate and hydroxide.

REQUIRED REAGENTS
(varies with sample characteristics)

Description	Unit	Cat. No
Alkalinity Reagent Set (about 100 tests)		22719-00
Includes: (1) 942-99, (1) 943-99, (1) 14388-01, (1) 14389-01		
Bromcresol Green-Methyl Red Powder Pillows	100/pkg	943-99
Phenolphthalein Powder Pillows	100/pkg	942-99
Sulfuric Acid Titration Cartridge, 1.600 N	each	14389-01
Sulfuric Acid Titration Cartridge, 0.1600 N	each	14388-01
Water, deionized	4 L	272-56

REQUIRED APPARATUS

Digital Titrator	each	16900-01
Flask, Erlenmeyer, 250-mL	each	505-46
Select one or more based on sample concentration:		
Cylinder, graduated, 10-mL	each	508-38
Cylinder, graduated, 25-mL	each	508-40
Cylinder, graduated, 50-mL	each	508-41
Cylinder, graduated, 100-mL	each	508-42

OPTIONAL REAGENTS

Alkalinity Standard Solution Voluette® Ampules, 0.500 N Na_2CO_3, 10-mL	16/pkg	14278-10
Bromcresol Green-Methyl Red Indicator Solution	100 mL MDB	23292-32
Bromphenol Blue Indicator Solution	100 mL MDB	14552-32
Bromphenol Blue Powder Pillows	100/pkg	14550-99
Buffer Powder Pillows, pH 3.7	25/pkg	14551-68
Buffer Powder Pillows, pH 4.5	25/pkg	895-68
Buffer Powder Pillows, pH 4.8	25/pkg	896-68
Buffer Powder Pillows, pH 5.1	25/pkg	897-68
Buffer Powder Pillows, pH 8.3	25/pkg	898-68
Methyl Purple Indicator Solution	100 mL MDB	21934-32
Phenolphthalein Indicator Solution, 5 g/L	100 mL MDB*	162-32
Sodium Thiosulfate Standard Solution, 0.1 N	100 mL MDB	323-32

* Contact Hach for larger sizes.

OPTIONAL APPARATUS

Description	Unit	Cat. No
Bottle, wash, poly, 500-mL	each	620-11
Clamp, 2-prong extension, 38-mm	each	21145-00
Clamp Holder	each	326-00
Demineralizer Assembly, 473-mL	each	21846-00
Delivery Tubes, with 180° hook	5/pkg	17205-00
Delivery Tubes, 90° with hook for TitraStir® Stir Plate	5/pkg	41578-00
Pipet, TenSette® 0.1 to 1.0 mL	each	19700-01
Pipet Tips for 19700-01 TenSette® Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 10-mL	each	14515-38
Pipet, volumetric, Class A, 20-mL	each	14515-20
Pipet, volumetric, Class A, 25-mL	each	14515-40
Pipet, volumetric, Class A, 50-mL	each	14515-41
Pipet, volumetric, Class A, 100-mL	each	14515-42
Pipet Filler, safety bulb	each	14651-00
sension™*1* Basic Portable pH Meter with electrode	each	51700-10
Support Ring Stand	each	563-00
TitraStir® Stir Plate, 115 Vac	each	19400-00
TitraStir® Stir Plate, 230 Vac	each	19400-10
Voluette® Ampule Breaker Kit	each	21968-00

3.1 Sample Collection, Preservation, and Storage

Correct sampling and storage are critical for accurate testing. Sampling devices and containers must be thoroughly clean to prevent carryover from previous samples. Preserve the sample properly; each procedure has information about sample preservation.

3.1.1 Collecting Water Samples

Use a clean container. Rinse the container several times with the water to be sampled before taking the sample. Document the location and procedure used for each sample taken. For example:

From a tap Take samples as close as possible to the source of the supply. This lessens the influence of the distribution system on the sample. Let the water run long enough to flush the system. Fill sample containers slowly with a gentle stream to avoid turbulence and air bubbles.

When testing well water, let the pump run long enough to draw fresh groundwater into the system. Collect a sample from a tap near the well.

From open waters Sample as near the middle of the body of water as is practical; at least several feet from the shore or edge of the tank.

Take the sample under the surface of the water. If you are using a capped container, submerge it before removing the cap.

3.1.1.1 Types of Containers

Table 1 lists recommended containers for specific parameters.

- **Polypropylene and Polyethylene** — These are the least expensive containers.
- **Quartz or TFE (tetrafluoroethylene, Teflon®)**—These are the best, and the most expensive.
- **Glass**—Glass provides a good general-purpose container. Avoid using soft-glass containers to collect samples to be tested for metals in the microgram-per-liter range.
  When determining silver, store samples in dark containers such as amber or brown glass.

Acid washing will thoroughly clean sample containers before use.

3.1.1.2 Acid Washing

If a procedure suggests acid washing, follow these steps:

a. Clean the glassware or plasticware with laboratory detergent. Phosphate-free detergent is best. (When determining phosphates, phosphate-free detergent *must* be used.)
b. Rinse well with tap water.
c. Rinse with a 1:1 hydrochloric acid solution or a 1:1 nitric acid solution. (Nitric acid is best when testing for lead or other metals.)
d. Rinse well with deionized water. For chromium, 12–15 rinses may be necessary. When determining ammonia and Kjeldahl nitrogen, the rinse water must be ammonia-free.

e. Air dry. Protect the glassware from fumes and other sources of contamination when storing.

Use chromic acid or chromium-free substitutes to remove organic deposits from glass containers. Afterward, rinse thoroughly with water to remove all traces of chromium.

Avoid introducing metal contaminants from containers, distilled water, or membrane filters.

3.1.1.3 Sample Splits

Samples must often be split or divided into separate containers for intra- or inter-laboratory use in studies, confirmation, alternative techniques, or maintaining additional sample for reference, or stability studies. It is very important that sample splits be done correctly.

- Collect a large volume of sample in a single container and transfer to smaller containers; do not fill the smaller containers individually from the water source.
- Thoroughly mix samples containing particulates or solids before splitting so that all the splits are homogeneous.
- If the sample requires filtering before analysis or storage, filter the entire sample before splitting.
- Use the same kind of container for all the splits.
- Analyze biologically active splits on the same day, or as close to the same day as is possible.
- Preserve all splits in the same way; if this is not done, the differing methods must be fully documented.
- When testing for volatile contaminants, fill containers samples to overflowing and cap carefully. Do not leave any headspace or air in the container.

3.1.2 Storage and Preservation

Because chemical and biological processes continue after collection, analyze the sample as soon as possible. This also reduces the chance for error and minimizes labor. When immediate analysis is not possible, the sample must be preserved. Preservation methods include pH control, chemical addition, refrigeration, and freezing.

Table 1 presents an overview of preservation methods and holding times for specific procedures.

You can preserve aluminum, cadmium, chromium, cobalt, copper, iron, lead, nickel, potassium, silver, and zinc samples for at least 24 hours by adding one Nitric Acid Solution Pillow 1:1 (Cat. No. 2540-98) per liter of sample. Check the pH with pH indicator paper or a pH meter to assure the pH is 2 or less. Add additional pillows if necessary. Adjust the sample pH prior to analysis by raising the pH to 4.5 with Sodium Hydroxide Standard Solution, 1 N or 5 N.

3.1.3 Correcting for Volume Additions

If you use a large volume of preservative or neutralizer, you must account for dilution by the acid added to preserve the sample, and/or the base used to adjust the pH to the range of the procedure. Make this correction as follows:

1. Determine the volume of initial sample, the volume of acid and base added, and the total final volume of the sample.
2. Divide the total volume by the initial volume.
3. Multiply the test result by this factor.

Example:

A one-liter sample was preserved with 2 mL of nitric acid. It was neutralized with 5 mL of 5 N sodium hydroxide. The result of the analysis procedure was 10.00 mg/L. What is the volume correction factor and correct result?

1. Total Volume $= 1000\text{ mL} + 2\text{ mL} + 5\text{ mL} = 1007\text{ mL}$
2. $\frac{1007}{1000} = 1.007 =$ volume correction factor
3. $10.0\text{ mg/L} \times 1.007 = 10.07\text{ mg/L} =$ correct result

Hach 1:1 Nitric Acid Pillows contain 2.5 mL of acid: correct for this volume.

Table 1 Required Containers, Preservation Techniques and Holding Times*

Parameter Name	Container**	Preservation*** ****	Maximum Holding Time*****
Table 1A - Bacterial Tests			
Coliform, fecal and total	P,G	Cool, 4 °C, 0.008% $Na_2S_2O_3$	6 hours
Fecal streptococci	P,G	Cool, 4 °C, 0.008% $Na_2S_2O_3$	6 hours
Table 1A - Aquatic Toxicity Tests			
Toxicity, acute and chronic	P, G	Cool, 4 °C	36 hours
Table 1B - Chemical Tests			
Acidity	P, G	Cool, 4 °C	14 days
Alkalinity	P, G	Cool, 4 °C	14 days
Ammonia	P, G	Cool, 4 °C, H_2SO_4 to pH<2	28 days
Biochemical oxygen demand (BOD)	P, G	Cool, 4 °C	48 hours
Boron	P, PFTE or quartz	HNO_3 to pH<2	6 months
Bromide	P, G	None required	28 days
Biochemical oxygen demand, carbonaceous	P, G	Cool, 4 °C	48 hours
Chemical oxygen demand	P, G	Cool, 4 °C, H_2SO_4 to pH<2	28 days
Chloride	P, G	None required	28 days
Chlorine, total residual	P, G	None required	Analyze immediately
Color	P, G	Cool, 4 °C	48 hours
Cyanide, total and amenable to chlorination	P, G	Cool, 4 °C, NaOH to pH>12, 0.6 g ascorbic acid******	14 days*******
Fluoride	P	None required	28 days
Hardness	P, G	HNO_3 to pH<2, H_2SO_4 to pH<2	6 months

Table 1 Required Containers, Preservation Techniques and Holding Times* (continued)

Parameter Name	Container**	Preservation***, ****	Maximum Holding Time*****
Hydrogen ion (pH)	P, G	None required	Analyze immediately
Kjeldahl and organic nitrogen	P, G	Cool 4 °C, H_2SO_4 to pH<2	28 days
Metals********			
Chromium VI	P, G	Cool, 4 °C	24 hours
Mercury	P, G	HNO_3 to pH<2	28 days
Metals, except boron, chromium VI and mercury	P, G	HNO_3 to pH<2	6 months
Nitrate	P, G	Cool, 4 °C	48 hours
Nitrate-nitrite	P, G	Cool 4 °C, H_2SO_4 to pH<2	28 days
Nitrite	P, G	Cool, 4 °C	48 hours
Oil and grease	G	Cool, 4 °C, HCl or H_2SO_4 to pH<2	28 days
Organic Carbon	P, G	Cool, 4 °C, HCl or H_2SO_4 or H_3PO_4 to pH<2	28 days
Orthophosphate	P, G	Filter immediately; Cool, 4 °C	48 hours
Oxygen, dissolved probe	G Bottle and top	None required	Analyze immediately
Oxygen, Winkler	G Bottle and top	Fix on site and store in dark	8 hours
48. Phenols	G only	Cool 4 °C, H_2SO_4 to pH<2	28 days
Phosphorus, elemental	G	Cool, 4 °C	48 hours
Phosphorus, total	P, G	Cool, 4 °C, H_2SO_4 to pH<2	28 days
Residue, Total	P, G	Cool, 4 °C	7 days
Residue, Filterable	P, G	Cool, 4 °C	7 days
Residue, Nonfilterable (TSS)	P, G	Cool, 4 °C	7 days
Residue, Settleable	P, G	Cool, 4 °C	48 hours
Residue, Volatile	P, G	Cool, 4 °C	7 days
Silica	P, PFTE or quartz	Cool, 4 °C	28 days
Specific Conductance	P, G	Cool, 4 °C	28 days
Sulfate	P, G	Cool, 4 °C	28 days
Sulfide	P, G	Cool 4 °C, add zinc acetate plus sodium hydroxide to pH>9	7 days
Sulfite	P, G	none required	Analyze immediately
Surfactants	P, G	Cool, 4 °C	48 hours
Temperature	P, G	None required	Analyze immediately
Turbidity	P, G	Cool, 4 °C	48 hours

* This table was adapted from Table II in the *Code of Federal Regulations*, July 1, 2000, Title 40, Part 136.3 (40 CFR 136.3), pages 23–25. Most organic tests are not included.

** Polyethylene (P) or glass (G), or PTFE Teflon

***Sample preservation should be performed immediately upon sample collection. For composite chemical samples each portion should be preserved at the time of collection. When use of an automated sampler makes it impossible to preserve each portion, then chemical samples may be preserved by maintaining at 4 °C until compositing and sample splitting is completed.

****When any sample is to be shipped by common carrier or sent through United States Mails, it must comply with the *Department of Transportation Hazardous Material Regulations* (49 CFR Part 172). The person offering such material for transportation is responsible for ensuring such compliance. For the preservation requirements of Table II, the Office of Hazardous Materials, Materials Transportation Bureau, Department of Transportation has determined that the Hazardous Materials Regulations do not apply to the following materials: Hydrochloric acid (HCl) in water solutions at concentrations of 0.04% by weight or less (pH about 1.96 or greater); Nitric acid (HNO_3) in water solutions at concentrations of 0.15% by weight or less (pH about 1.62 or greater); Sulfuric acid (H_2SO_4) in water solutions at concentrations of 0.35% by weight or less (pH about 1.15 or greater); and Sodium hydroxide (NaOH) in water solutions at concentrations of 0.080% by weight or less (pH about 12.30 or less).

*****Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still be considered valid. Samples may be held for longer periods only if the permittee, or monitoring laboratory has data on file to show that the specific types of samples under study are stable for the longer time, and has received a variance from the Regional Administrator under §136.3(e). Some samples may not be stable for the maximum time period given in the table. A permittee or monitoring laboratory is obligated to hold the sample for a shorter time if knowledge exists to show that this is necessary to maintain sample stability. See §136.3(e) for details. The term "analyze immediately" usually means within 15 minutes or less after sample collection.

******Should only be used in the presence of residual chlorine.

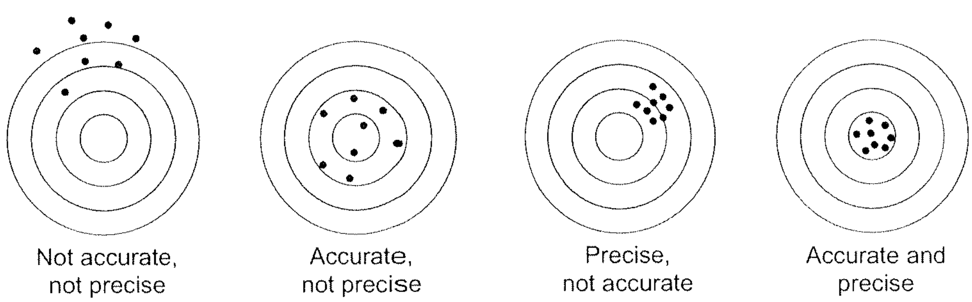
*******Maximum holding time is 24 hours when sulfide is present. Optionally all samples may be tested with lead acetate paper before pH adjustments in order to determine if sulfide is present. If sulfide is present, it can be removed by the addition of cadmium nitrate powder until a negative spot test is obtained. The sample is filtered and then NaOH is added to pH 12.

********Samples should be filtered immediately on-site before adding preservative for dissolved metals.

3.2 Checking for Accuracy and Precision

Accuracy defines the closeness of a test result to the true value. Precision defines the closeness of repeated measurements to each other. Although precise results suggest accuracy, they can be inaccurate. Both the accuracy and the precision of test results can be evaluated by using standard additions or standard solutions.

Figure 1 Precision and Accuracy Illustrated



3.2.1 Standard Solutions

A standard solution may be ordered as a prepared reagent or it may be made in the laboratory. It is a solution of a known composition and concentration. The accuracy of your analysis system may be checked by using a standard solution in place of the sample water in a procedure.

3.2.2 Standard Additions

Standard Additions is a common technique for checking test results. Other names are "spiking" and "known additions." The technique can test for interferences, bad reagents, faulty instruments, and incorrect procedures.

Perform Standard Additions by adding a small amount of a standard solution to your sample and repeating the test. Use the same reagents, equipment, and technique. You should get about 100% recovery. If not, you have an identifiable problem.

If Standard Additions works for your test, a Standard Additions Method section will be in the procedure under Accuracy Check. Follow the detailed instructions given.

If you get about 100% recovery for each addition, everything is working properly and your results are correct.

If you don't get about 100% recovery for each addition, a problem exists. You can tell if you have an interference. Repeat the Standard Additions using deionized water as your sample. If you get about 100% recovery for each addition, you have an interference.

If you didn't get good recoveries with the deionized water, use the following checklist to find the problem:

1. Check to see that you are following the procedure exactly:
   a. Are you using the proper reagents in the proper order?
   b. Are you waiting the necessary time for color to develop?
   c. Are you using the correct glassware?
   d. Is the glassware clean?
   e. Does the test need a specific sample temperature?
   f. Is the sample's pH in the correct range?

Hach's written procedure should help you to answer these questions.

2. Check the performance of your instrument. Follow the instructions in the Service Checks section of the instrument manual.
3. Check your reagents. Repeat the Standard Additions using new, fresh reagents. If your results are good, the original reagents were faulty.
4. If nothing else is wrong, the standard is almost certainly defective. Repeat the Standard Additions with a new standard.
5. If you still cannot identify the problem, you may need some extra help. Please call Hach's Technical Support Group at 800-227-4224 (U.S.A.) or 303-669-3050. A representative will be happy to help you.

3.2.3 Troubleshooting a Test When Results are in Doubt

If the results from any Hach chemistry are in doubt, troubleshoot them as follows:

1. Run a proof-of-accuracy check. Take a standard solution, which has a known concentration, through the same steps as the original sample. Include sampling and storage, digestion and colorimetric determination, if applicable. If the results of the standard solution check are correct, skip to *step 4* below. If there is a variation in the expected results, go to *step 2.*

2. If the standard solutions check does not match the expected results, check the instrument set-up and method procedure as follows:
   a. Verify that the correct program number for the test being performed is selected.
   b. Verify that the units of concentration of the standard match the displayed units. (One of the alternative forms of the analyte may be in the display.) For example: Molybdenum may be shown as Mo instead of MoO_4.
   c. Verify that the sample cells called for in the procedure are the ones being used.
   d. Verify that the reagents are correct for the sample size being analyzed.
   e. Where applicable, verify that the reagent blank value stored is for the current procedure. It may be from a previous lot of reagents and therefore not representative of the current reagent lot.
   f. Where applicable, verify the calibration curve adjustment (Standard Adjust) currently in use. The factory-stored default calibration should be used initially to check the standard.
   g. Where applicable, verify that the dilution factor option is correct.

If the instrument setup is correct and the method procedure specifics are being followed correctly, go to *step 3*.

3. If the standard solution check does not match the expected results, check the reagents used in the test and the analytical technique as follows:
   a. Determine the age of the reagents used in the test. While most Hach reagents have a long shelf life, many factors affect this (i.e., storage temperature, storage conditions, microbial contamination). Replace suspect reagents and run the standards check again.
   b. Run a deionized or distilled water blank through the entire process; include sampling and storage, digestion, and colorimetric determination. Some chemicals will add a small amount of color to a test; this is not considered unusual. However, color development in excess of 10% of the range of the test may indicate a problem with one of the reagents or the dilution water.
   c. To troubleshoot the procedure, delete the parts one by one. First, using the standard solution, omit preservation and storage, doing only digestion and colorimetry. If this analysis is correct, examine the procedure used to store the sample. Ensure that it is the procedure prescribed for the chosen parameter. If the sample is acidified for storage, be sure the correct acid is used and the sample is adjusted to the proper pH level before testing.

      If the standards check is still incorrect, run the standard on just the colorimetry. If the results are correct, examine the digestion procedure. Ensure that the amount of reagents used and the pH after the digestion are correct for the procedure. (See the procedure for the parameter in question.)

4. If the standard solution gives a correct value, but the results of the sample measurement are questionable, there may be an interference in the sample. To check for an interference:
   a. Spike the sample. Use a standard addition test instead of a standard solution test to include any possible interferences.

To two cells containing fresh sample water, add an amount of standard equal to two times the concentration of the sample. Process both samples using the same reagents, instruments, and technique. The spiked sample should show an increase equal to the amount of standard added. Calculate percent recovery as shown below. Ideally, the results should be 100%, with results from 90 to 110% considered acceptable. Refer to the procedure notes for possible interferences and ways to eliminate them.

b. Run a series of dilutions on the sample. Make sure your sample is within the range of the test. A sample out of range for the method may give erroneous results because of under- or over-development of the color, excess turbidity, or even sample bleaching. Run a series of dilutions to check for this possibility.

   Because it may not be feasible to determine the cause of the interference, diluting the sample past the point of interference is often the most economical and efficient means of getting the correct result. If it is not possible to dilute out an interference without diluting out the parameter to be measured, use a different method, such as a different chemistry or an ion-selective electrode to measure the parameter.

Calculating percent recovery:

1. Measure the unknown sample concentration.
2. Calculate the theoretical concentration of the spiked sample using the following formula:

$$\text{Theoretical Concentration} = \frac{(C_u \times V_u) + (C_s \times V_s)}{V_u + V_s}$$

Where:

C_u = measured concentration of the unknown sample
V_u = volume of the unknown sample
C_s = concentration of the standard
V_s = volume of the standard

3. Measure the spiked sample concentration.
4. Divide the spiked sample concentration by the theoretical concentration and multiply by 100.

For example:

A sample was tested for manganese and the result was 4.5 mg/L. A separate 97-mL portion of the same sample was spiked with 3 mL of a 100 mg/L standard solution of manganese. This spiked solution was tested again for manganese using the same method. The result was 7.1 mg/L.

The theoretical concentration of the spiked sample is:

$$\frac{(4.5\text{ mg/L} \times 97\text{ mL}) + (100\text{ mg/L} \times 3\text{ mL})}{97\text{ mL} + 3\text{ mL}} = 7.4\text{ mg/L}$$

The percent spike recovery is:

$$\frac{7.1\text{ mg/L}}{7.4\text{ mg/L}} \times 100 = 96\%$$

USEPA Calculation

The USEPA requires a more stringent calculation for percent recovery. This formula calculates the percent recovery only for the standard added to the spiked sample and yields a lower value than the above calculation. A complete explanation for the USEPA formula is in *USEPA Publication SW-846*. The USEPA percent recovery formula is:

$$\%R = \frac{100(X_s - X_u)}{K}$$

Where:

X_s = measured value of the spiked sample
X_u = measured value for the unspiked sample, adjusted for the dilution of the spike volume
K = known value of the spike in the sample

Example:

A sample measures 10 mg/L. A separate 100-mL portion of the sample was spiked with 5 mL of a 100-mg/L standard solution. The spiked solution was measured by the same method as the original sample. The result was 13.7 mg/L.

$$X_s = 13.7 \text{ mg/L}$$

$$X_u = \frac{10 \text{ mg/L} \times 100 \text{ mL}}{105 \text{ mL}} = 9.5 \text{ mg/L}$$

$$K = \frac{5 \text{ mL} \times 100 \text{ mg/L}}{105 \text{ mL}} = 4.8 \text{ mg/L}$$

$$\%R = \frac{100 \times (13.7 \text{ mg/L} - 9.5 \text{ mg/L})}{4.8 \text{ mg/L}} = 88\%$$

Acceptable percent recovery values are 80-120%.

3.2.4 Adjusting the Standard Curve

Note: *Not available on all instruments.*

Hach instruments contain programs permanently installed in memory. A program usually includes a pre-programmed calibration curve. Each curve is the result of an extensive calibration performed under ideal conditions and is normally adequate for most testing. Deviations from the curve can occur from using compromised testing reagents, defective sample cells, incorrect test procedure, incorrect technique, or other correctable causes. Interfering substances or other causes may be beyond the analyst's control.

In some situations, using the pre-programmed curve may not be convenient:

- Running tests where the reagents are highly variable from lot to lot.
- Running tests where frequent calibration curve checks are required.
- Testing samples which give a consistent test interference.

Consider the following before adjusting the calibration curve:

- Will future test results be improved by adjusting the curve?
- Are interfering substances consistent in all the samples that you will test?
- Any estimated detection limit, sensitivity, precision, and test range information provided with the procedure may not apply to an adjusted curve calibration.

The calibration curves can be adjusted by following the steps found in the test procedure. Generally, you add test reagents to a blank and standard solution. Working carefully is important. After the adjustment, it is wise to run standard solutions of several concentrations to make sure the adjusted curve is satisfactory. Performing standard additions on typical samples may also help determine if the adjusted curve is acceptable.

Think of adjusting a measurement as a two-step process. First, the instrument measures the sample using the pre-programmed calibration. Second, it multiplies this measurement by an adjustment factor. The factor is the same for all concentrations The instrument will remember the factor until the program is exited and will display the standard adjustment icon when it is used. You can return to the pre-programmed curve any time by selecting the Hach Program from the main menu.

3.3 Interferences

Interferences are contaminants in a sample that are capable of causing changes in color development, turbidity, or unusual colors and odors, thereby creating errors in your results. A list of common interferences is included in each procedure. Hach reagents are formulated to eliminate many interferences; you can remove others by pretreating the sample as instructed in the procedure.

Test strips are available for many of the common interferences. These can be conveniently used to screen samples for the presence of interferences.

If you get test results that you feel are inaccurate, if you get an unexpected color, or if you notice an unusual odor or turbidity, repeat the test on a sample diluted with deionized water. (See *Section 2.7 Sample Dilution*.) Correct the results for the dilution, and compare them with those from your original test. If they differ significantly, make a second dilution and check it against the first. Repeat the dilutions until you get the same result (after volume corrections) twice in succession.

For more information on interferences, see *Section 3.2.2 Standard Additions*. The *APHA Standard Methods* book, an excellent reference for the water analyst, also covers interferences in its "General Introduction."

pH Interference

Chemical reactions are often pH dependent. Hach reagents contain buffers to adjust the pH of the sample to the correct range. However, the reagent buffer may not be strong enough for samples that are highly buffered or have an extreme pH.

The *Sampling and Storage* section of each procedure gives the pH range for that test.

Before testing, adjust the sample to the proper pH as instructed in the procedure, or by following these steps:

1. Measure the pH of your analyzed sample with a pH meter.

   ***Note:** Use pH paper when testing for chloride, potassium, or silver to avoid contamination.*

2. Prepare a reagent blank using deionized water as the sample. Add all reagents called for in the procedure. Timer sequences, etc., may be ignored. Mix well.
3. Measure the pH of the reagent blank with a pH meter.
4. Compare the pH values of your analyzed sample with the reagent blank.
5. If there is little difference in the values of your analyzed sample and the reagent blank, then pH interference is not the problem. Follow the *Accuracy Check* for the specific procedure to more clearly identify the problem.

6. If there is a large difference between the value of your analyzed sample and the reagent blank, adjust the sample pH to the value of the reagent blank. Adjust the sample pH to this same pH for all future samples before analysis. Use the appropriate acid, usually nitric acid, to lower the pH. Use the appropriate base, usually sodium hydroxide, to raise the pH. Adjust the final result for any dilution caused by adding acid or base; see *Correcting for Volume Additions*.
7. Analyze the sample as before.
8. Some purchased standards may be very acidic and will not work directly with Hach procedures. Adjust the pH of these standards as described above. Adjust the final concentration of the standard for the dilution. The Hach standard solutions suggested in the procedures are formulated so that no pH adjustment is necessary.

3.4 Method Performance

3.4.1 Estimated Detection Limit (EDL)

Ranges for chemical measurements have limits. The lower limit is important because it determines whether a measurement is different from zero. Many experts disagree about the definition of this detection limit, and determining it can be difficult. The *Code of Federal Regulations* (40 CFR, Part 136, Appendix B) provides a procedure to determine the "Method Detection Limit" or MDL. The MDL is the lowest concentration that is different from zero with a 99% level of confidence. A measurement below this MDL is highly suspect.

The MDL is not fixed; it varies for each reagent lot, instrument, analyst, sample type, etc. Therefore, a published MDL may be a useful guide, but is only accurate for a specific set of circumstances. Each analyst should determine a more accurate MDL for each specific sample matrix using the same equipment, reagents, and standards that will routinely be used for measurements.

Hach provides a sensitivity value (concentration change equivalent to an absorbance change of 0.010 abs) as an estimate of the lower detection limit of each test. The sensitivity value may be treated as an EDL for the purposes of MDL determination. It can be considered a good starting concentration when determining a MDL. **Do not use the EDL for MDL**. The conditions for MDL determination must be exactly the same as the conditions used for analysis. The EDL may be useful to the analyst as a starting point in determining a MDL, or as a way to compare methods. Measurements below the EDL may also be valuable because they can show a trend, indicate the presence of analyte and/or provide statistical data. However, these values have a large uncertainty.

3.4.2 Method Detection Limit (MDL)

This method is in accordance with the USEPA definition in 40 CFR, Part 136, Appendix B in the 7-1-94 edition. The USEPA defines the method detection limit (MDL) as the minimum concentration that can be determined with a 99% level of confidence that the true concentration is greater than zero. Since the MDL will vary from analyst to analyst, it is important that the MDL be determined under actual operating conditions.

The procedure for determining MDL is based on replicate analyses at a concentration 1 to 5 times the estimated detection limit. The MDL value is calculated from the standard deviation of the replicate study results multiplied by the appropriate Student's *t* value for a 99% confidence interval. For this definition, the MDL does not account for variation in sample composition and can only be achieved under ideal conditions.

1. Estimate the detection limit. Use the Hach sensitivity value stated in the *Method Performance* section of the analysis procedure.
2. Prepare a laboratory standard of the analyte, 1 to 5 times the estimated detection limit, in deionized water that is free of the analyte.
3. Analyze at least seven portions of the laboratory standard and record each result.
4. Calculate the average and the standard deviation(*s*) of the results.
5. Compute the MDL using the appropriate Student's *t* value (see table below) and the standard deviation value:

$$MDL = \text{Students } t \times s$$

Number of Test Portions	Student's *t* Value
7	3.143
8	2.998
9	2.896
10	2.821

For example:

The EDL for measuring iron using the FerroZine® method is 0.003 mg/L. An analyst accurately prepared 1 liter of a 0.010 mg/L (about 3x the EDL) laboratory standard by diluting a 10-mg/L iron standard in iron-free deionized water.

Eight portions of the standard were tested according to the FerroZine method with the following results:

Sample #	Result (mg/L)
1	0.009
2	0.010
3	0.009
4	0.010
5	0.008
6	0.011
7	0.010
8	0.009

Using a calculator program, the average concentration = 0.010 mg/L and the standard deviation (*s*) = 0.0009 mg/L

Based on the USEPA's definition, calculate the MDL as follows:

MDL for FerroZine method = 2.998 (Student's *t*) x 0.0009 (*s*)

MDL = 0.003 mg/L (agrees with initial estimate)

Note: *Occasionally, the calculated MDL may be very different than Hach's estimate of the detection limit. To test how reasonable the calculated MDL is, repeat the procedure using a standard near the calculated MDL. The average result calculated for the second MDL derivation should agree with the initial calculated MDL. Refer to 40 CFR, Part 136, Appendix B (7-1-94), pages 635–637 for detailed procedures to verify the MDL determination.*

Run a laboratory blank, containing deionized water without analyte, through the test procedure to confirm that the blank measurement is less than the calculated MDL. If the blank measurement is near the calculated MDL, repeat the MDL procedure using a separate blank for analysis for each portion of standard solution analyzed. Subtract the average blank measurement from each standard and use the corrected standard values to calculate the average and standard deviation used in the MDL.

3.4.3 Precision

Every measurement has some degree of uncertainty. Just as a ruler with markings of 1 mm leaves some doubt as to the exact length of a measurement, chemical measurements also have some degree of uncertainty. The quality of the entire calibration curve determines the precision.

Uncertainty in chemical measurements may be due to systematic errors and/or random errors. A systematic error is a mistake that is always the same for every measurement made. For example, a blank can add to each measurement for a specific compound, giving consistently high results (a positive bias). Random errors are different for every test and can add either a positive or negative variation in response. Random errors are most often caused by variation in analytical technique. Hach chemists work hard to eliminate systematic errors in Hach procedures using Hach reagents, but response variation occurs in all chemical measurements.

3.4.4 Estimating Precision

The method performance section in each procedure provides an estimate of the procedure's precision. Two types of estimates are used throughout this book. Most of the procedures use a *replicate analysis* estimate, based on real data. For precision determined in this manner, the 95% confidence interval of the distribution is reported. Some newer procedures use a 95% or 99% *confidence interval*, which is based on the calibration data for that particular chemistry.

In replicate analysis, a Hach chemist prepares a specific concentration of the analyte in a deionized water matrix. The standard is then analyzed seven individual times on a single instrument with the two reagent lots originally used in the calibration (a total of 14 samples). A standard deviation of each of the two sets of seven values is calculated, and the worst-case 95% confidence interval of the distribution is reported in the method. The reported value provides an estimate of the "scatter" of results at a particular point in the calibration curve.

In either case, it is important to realize that the estimates are based on a deionized water matrix. Precision on real samples with varying matrices can be quite different from these estimates.

If the concentration obtained from running a standard solution does not fall within the stated precision, please refer to *Section 3.2.3 Troubleshooting a Test When Results are in Doubt.*

3.4.5 Sensitivity

Hach's definition of sensitivity is the change in concentration (ΔConcentration) for a 0.010 change in absorbance (ΔAbs).

Use sensitivity when comparing different methods. For example, Hach has three DR/2500 methods for determining iron:

Iron Analysis Method	Portion of Curve	ΔAbs	ΔConcentration
FerroVer	Entire range	0.010	0.022 mg/L
FerroZine	Entire range	0.010	0.009 mg/L
TPTZ	Entire range	0.010	0.012 mg/L

Notice that the FerroZine method has the greatest sensitivity of the three methods because it will measure the smallest change in concentration. The technical definition of sensitivity comes from a calibration curve with Abs on the x-axis and concentration on the y-axis.

1. If the calibration is a line, the sensitivity is the slope of the line multiplied by 0.010.
2. If the calibration is a curve, the sensitivity is the slope of the tangent line to the curve at the concentration of interest multiplied by 0.010.

The sensitivity value is also used as an estimate of the lower limit of the test. The value may be used as a starting point in determining MDL.

3.5 Preparing a Calibration Curve

Note: *Calibration curves are recommended when using a non-Hach instrument or where required by a regulator.*

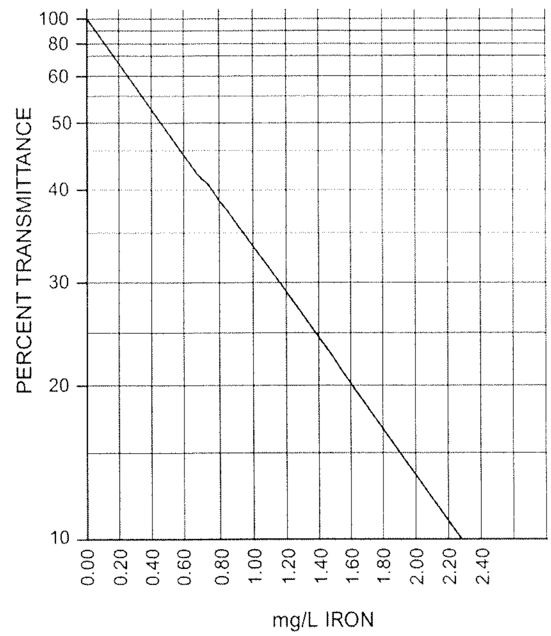
1. Prepare five or more standards of known concentration that cover the expected range of the test. Run tests as described in the procedure on each prepared standard. Then pour the customary volume of each known solution into a separate clean sample cell of the type specified for your instrument.
2. Select the proper wavelength. Standardize (zero) the instrument using an untreated water sample or a reagent blank, whichever the procedure instructs you to use.
3. Measure and record the absorbance of the known solutions within the time constraints detailed in the procedure. To use absorbance vs. concentration, see *Section 3.5.2 Absorbance Versus Concentration Calibration.*

3.5.1 %T Versus Concentration Calibration

If measuring %T, use semilogarithmic graph paper and plot %T (vertical scale) versus concentration (horizontal scale). For *Figure 2*, iron standard solutions of 0.1, 0.2, 0.4, 0.8, 1.2, 1.6 and 2.0 mg/L were measured on a Spectronic® 20* at 500 nm using half-inch test tubes. Results were plotted and the calibration table values were extrapolated from the curve (*Table 2*).

* Spectronic is a registered trademark of Thermo Electron Corporation

Figure 2 Semilogarithmic Calibration Curve



To convert %T readings to concentration, prepare a table such as *Table 2* and select the appropriate line from the "%T Tens" column and the appropriate column from the "%T Units" columns. The %T Ten value is the first number of the % transmittance reading and the %T Units value is the second number of the % transmittance reading. For example, if the instrument reading was 46%, the 40 line in the %T Tens column and the 6 column in the %T Units would be selected. The cell where these two intersect (0.78 mg/L) is the iron concentration of the sample.

Table 2 Calibration Table

	Absorbance Units									
Absorbance Tens	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
0	–	–	–	–	–	–	–	–	–	–
10	2.30	2.21	2.12	2.04	1.97	1.90	1.83	1.77	1.72	1.66
20	1.61	1.56	1.51	1.47	1.43	1.39	1.35	1.31	1.27	1.24
30	1.20	1.17	1.14	1.11	1.08	1.04	1.02	.99	.97	.94
40	.92	.89	.87	.84	.82.	.80	.78	.76	.73	.71
50	.69	.67	.65	.64	.62	.60	.58	.56	.55	.53
60	.51	.49	.48	.46	.45	.43	.42	.40	.39	.37
70	.36	.34	.33	.32	.30	.29	.28	.26	.25	.24
80	.22	.21	.20	.19	.17	.16	.15	.14	.13	.12
90	.11	.09	.08	.07	.06	.05	.04	.03	.02	.01

3.5.2 Absorbance Versus Concentration Calibration

If absorbance values are measured, plot the results on linear graph paper. Plot the absorbance value on the vertical axis and the concentration on the horizontal axis.

Plot increasing absorbance values from bottom to top. Plot increasing concentration values from left to right. Values of 0.000 absorbance units and 0 concentration will begin at the bottom left corner of the graph. A calibration table can be extrapolated from the curve or the concentration values can be read directly from the graph. Or determine an equation for the line using the slope and y-intercept.

3.6 Adapting Procedures to Other Spectrophotometers

Hach procedures may be used with other spectrophotometers, if calibration curves are made that convert absorbance to concentration. Regardless of the spectrophotometer used, prepare the sample and calibration standards following the Hach procedure and use the optimum wavelength used in the Hach procedure.

To calibrate for a given analyte, a series of standards are prepared and measured to establish the calibration curve. The absorbance vs. concentration is plotted on linear graph paper (as described in *Section 3.5.2 Absorbance Versus Concentration Calibration*). Points on the graph are connected with a smooth line (curved or straight). If necessary, use the curve to make a calibration table.

3.6.1 Selecting the Best Wavelength

When developing a new procedure, or using procedures that are sensitive to wavelength, it is normal to select the wavelength where the instrument gives the greatest absorbance (see *Figure 3*). Because Hach chemists have selected the best wavelength for the procedures in this book; selecting the wavelength is not necessary for most procedures.

3.6.1.1 General steps to select the best wavelength on a spectrophotometer:

1. Refer to the instrument manual for specific instructions for wavelength adjustments.
2. Select single wavelength adjustment.
3. Enter a wavelength in the range of interest.

Note: *Sample color provides a good indication of what wavelength region to use. A yellow solution absorbs light in the 400–500 nm region. A red solution absorbs light between 500–600 nm. A blue solution absorbs light in the 600–700 nm range.*

4. Prepare the sample and blank for analysis. Fill the appropriate sample cells with the blank and the reacted sample solution.
5. Place the blank in the cell holder. Zero the instrument.
6. Place the prepared sample into the cell holder. Read the absorbance level.
7. Increase the wavelength so it is at least 100 nm greater than the range of interest. Re-zero as in step *5*. Measure and record the absorbance of the sample.
8. Repeat, decreasing the wavelength by 50 nm. Re-zero, then measure and record the absorbance at each increment. Continue this process throughout the wavelength range of interest. Note the wavelength of greatest absorbance. (See *Table 3*.)

Table 3 Example

Wavelength	Absorbance
550 nm	0.477

Table 3 Example

Wavelength	Absorbance
500 nm	0.762
450 nm	0.355
400 nm	0.134

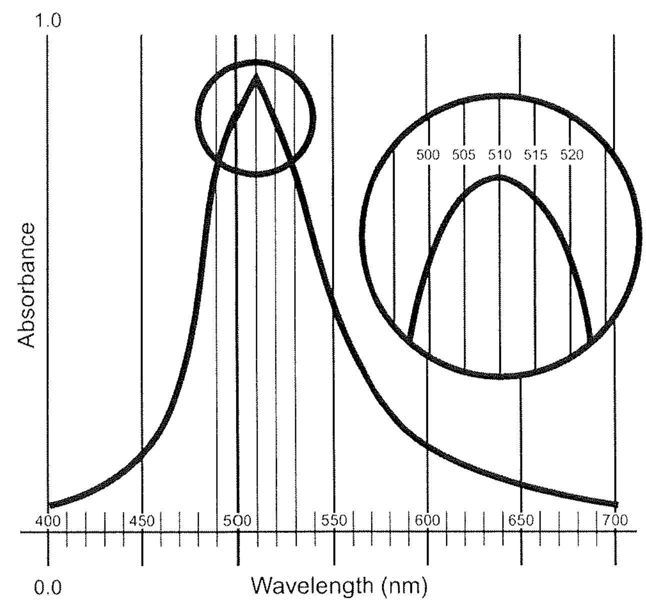
9. Adjust the wavelength to 50 nm more than the highest absorbance point on the initial search (step *8*). Re-zero as in step *5*.
10. Measure and record the absorbance. Repeat, decreasing the absorbance in 5-nm steps. Re-zero, then measure and record the absorbance at each increment. Continue until the entire range of interest is measured (see *Table 4*).

Table 4 Example

Wavelength	Absorbance
520 nm	0.748
515 nm	0.759
510 nm	0.780
505 nm	0.771
500 nm	0.771
495 nm	0.651
490 nm	0.590

Check to be sure there is enough difference in absorbance between samples with low and high analyte concentrations by measuring two sample solutions that contain the expected low and high concentrations of analyte at the optimum wavelength. The change in absorbance caused by increases/decreases in concentration depends on the sensitivity of the procedure and the chemistry. Chemistries with small absorbance changes are less sensitive, but tend to have larger ranges. Chemistries with large absorbance changes are more sensitive, but tend to have smaller ranges.

Figure 3 Selecting the Best Wavelength



Adapting a Buret Titration for Use With a Digital Titrator

Any standard titration procedure that uses a buret can be adapted to the Digital Titrator by using the following procedure.

1. From *Table 5* on page *39*, select a titration cartridge having the same active ingredient as the buret solution.
2. Determine the approximate number of digits required. The Digital Titrator dispenses 1 mL per 800 digits on the counter. Using the following equation, determine the digits required for your buret method.

$$\text{Digits Required} = \frac{N_t \times mL_t \times 800}{N_c}$$

Where:

N_t = Normality of buret titrant

mL_t = milliliters of buret titrant required for an average titration

N_c = Normality of Digital Titrator cartridge.

If the number of digits required is within the range of 70 to 350, you can use the procedure as written, substituting the Digital Titrator directly for the buret.

Or, if the number of digits is outside of this range, make the following modifications:

a. If the number of digits required is greater than 350, decrease the sample size to save titrant.

b. If the number of digits required is less than 70, increase the sample size to increase precision.

c. If the sample size is altered, adjust the amount of buffering or indicating reagents by the same proportion.

3. When using the Digital Titrator for your buret method, note the number of digits required for a sample titration. To convert the digits required to the equivalent number of milliliters for a buret method, calculate:

$$\text{Equivalent Buret Milliliters} = \text{Digits Required} \times \frac{N_c}{800 \times N_t}$$

If the sample size was changed, adjust the equivalent buret milliliters accordingly. If the sample size was increased, reduce the equivalent buret milliliters; if the sample size was reduced, increase the equivalent buret milliliters. Multiply the equivalent buret milliliters by any normally used factors to calculate concentration in oz./gal, g/L, etc.

Example: Adapt a buret procedure that normally requires about 20 mL of a 0.4 N titrant to the Digital Titrator. Try an 8.0 N titration cartridge. The first equation above gives:

$$\text{Digits Required} = \frac{0.4 \times 20 \times 800}{8.0} = 800 \text{ digits}$$

Because this would use excessive titrant, reduce the sample size to one-fourth its normal size to reduce the digits required to 200, well within the recommended range.

Upon completion of the titration using the smaller sample size, calculate the equivalent buret milliliters by the second equation above.

If 205 were the digits required:

$$\text{Equivalent Buret Milliliters} = \frac{205 \times 8.0}{800 \times 0.4} = 5.13 \text{ mL}$$

Multiply the resulting 5.13 mL by four to account for the reduction in sample size and give the true equivalent buret milliliters of 20.5 mL. If the buret method called for multiplying the number of milliliters of titrant by a factor to calculate the concentration of a sample component, then multiply 20.5 by that factor.

Table 5 Titration Cartridges

Description	Cat. No.
Bismuth Nitrate, 0.0200 M	24345-01
CDTA, 0.800 M, HexaVer	14403-01
Ceric Standard Solution, 0.5N	22707-01
EDTA, 0.0800 M, TitraVer	14364-01
EDTA, 0.142 M	14960-01
EDTA, 0.714 M	14959-01
EDTA, 0.800 M, TitraVer	14399-01
FEAS, ferrous ethylenediammonium sulfate, 0.00564 N	22923-01
Hydrochloric Acid, 8.00 N	14390-01
Iodate-Iodide, potassium, 0.3998 N	14961-01
Iodate-Iodide, potassium, 1.00 N	22944-01
Magnesium Chloride, 0.0800 N	20625-01
Mercuric Nitrate, 0.2256 N	14393-01
Mercuric Nitrate, 2.256 N	921-01
Mercuric Nitrate, 2.57 N	23937-01
PAO, phenylarsine oxide, 0.00451 N	22599-01

Table 5 Titration Cartridges (continued)

Description	Cat. No.
PAO, phenylarsine oxide, 0.0451 N	21420-01
Potassium Dichromate, 1.00 N	21971-01
Silver Nitrate, 0.2256 N	14396-01
Silver Nitrate, 1.128 N	14397-01
Sodium Hydroxide, 0.1600 N	14377-01
Sodium Hydroxide, 0.1612 N	24280-02
Sodium Hydroxide, 0.3636 N	14378-01
Sodium Hydroxide, 0.9274 N	14842-01
Sodium Hydroxide, 1.600 N	14379-01
Sodium Hydroxide, 3.636 N	14380-01
Sodium Hydroxide, 0.9274 N	14842-01
Sodium Hydroxide, 8.00 N	14381-01
Sodium Thiosulfate, 0.00451 N	24086-01
Sodium Thiosulfate, 0.0451 N	24095-01
Sodium Thiosulfate, 0.02256 N	24091-01
Sodium Thiosulfate, 0.0250 N	24093-01
Sodium Thiosulfate, 0.113 N	22673-01
Sodium Thiosulfate, 0.2000 N	22675-01
Sodium Thiosulfate, 0.2068 N	22676-01
Sodium Thiosulfate, 2.00 N	14401-01
Sodium Vanadate, 0.25 N	22949-01
Sulfuric Acid, 0.1600 N	14388-01
Sulfuric Acid, 1.600 N	14389-01
Sulfuric Acid, 8.00 N	14391-01
TitraVer, 0.0716 M	20817-01
TitraVer, 0.716 M	20818-01

3.7 Comparison of International Drinking Water Guidelines

Table 6 Comparison of International Drinking Water and FDA Bottled Water Guidelines*

Parameter	USEPA** Maximum Contaminant Level (MCL)	Canada*** Maximum Acceptable Concentration	EEC**** Maximum Admissible Concentration	Japan***** Maximum Admissible Concentration	WHO****** Guideline	Bottled Water U.S. Federal Drug Administration Level
Aluminum	0.05–0.2 mg/L*******		0.2 mg/L	0.2 mg/L	0.2 mg/L	
Ammonium			0.5 mg/L	No standard	1.5 mg/L	
Antimony	0.006 mg/L		0.01 mg/L	0.002 mg/L********	0.005 mg/L	
Arsenic	0.05 mg/L	0.025 mg/L	0.05 mg/L	0.01 mg/L	0.01 mg/L	0.05 mg/L
Barium	2.0 mg/L	1.0 mg/L	No standard	No standard	0.7 mg/L	2.0 mg/L
Boron		5.0 mg/L	1.0 mg/L	0.2 mg/L[8]	0.3 mg/L	
Cadmium	0.005 mg/L	0.005 mg/L	0.005 mg/L	0.01 mg/L	0.003 mg/L	0.005 mg/L
Chloride	250 mg/L[7]	250 mg/L	250 mg/L	200 mg/L	250 mg/L	
Chromium	0.1 mg/L	0.05 mg/L	0.05 mg/L	0.05 mg/L	0.05 mg/L	0.1 mg/L
Coliforms, total Organisms/100 mL	≤% positive	0	0 or MPN ≤1	0	0	≤1 MF
Coliforms (*E. coli*) Organisms/100 mL	0	0	0	0	0	
Color	15 cu[7]	15 cu	20 mg Pt-Co/L	5 cu	15 cu	<15 cu
Copper	1.3 mg/L[7]	1.0 mg/L	2.0 mg/L	1.0 mg/L	1–2 mg/L	1.0 mg/L
Cyanides	0.2 mg/L	0.2 mg/L	0.05 mg/L	0.01 mg/L	0.07 mg/L	
Fluoride	2.0-4.0 mg/L[7]	1.5 mg/L	0.7-1.5 mg/L	0.8 mg/L	1.5 mg/L	
Hardness			50 mg/L	300 mg/L		
Iron	0.3 mg/L[7]	0.3 mg/L	0.2 mg/L	0.3 mg/L	0.3 mg/L	
Lead	0.015 mg/L	0.01 mg/L	0.01 mg/L	0.05 mg/L	0.01 mg/L	0.005 mg/L
Manganese	0.05 mg/L	0.05 mg/L	0.05 mg/L	0.01–0.05 mg/L	0.1–0.5 mg/L	
Mercury	0.002 mg/L	0.001 mg/L	0.001 mg/L	0.0005 mg/L	0.001 mg/L	0.002 mg/L
Molybdenum				0.07 mg/L	0.07 mg/L	
Nickel	0.1 mg/L		0.02 mg/L	0.01 mg/L[8]	0.02 mg/L	
Nitrate/Nitrite, total	10.0 mg/L as N			10.0 mg/L as N		10 mg/L as N
Nitrates	10.0 mg/L as N	10.0 mg/L as N	50 mg/L	10 mg/L as N	50 mg/L as NO_3^-	
Nitrites	1 mg/L as N	3.2 mg/L	0.1 mg/L	10 mg/L	3 mg/L as NO_2^-	1 mg/L as N
Odor	3 TON*********		2 dilution no. @ 12 °C; 3 dilution no. @ 25 °C.	3 TON		
pH	6.5–8.5	6.5–8.5	6.5–9.5	5.8–8.6	6.5–8.5	
Phosphorus			5 mg/L	No Standard		
Phenols		0.002 mg/L	0.5 µg/L C_6H_5OH	0.005 mg/L		
Potassium			12 mg/L	No Standard		
Selenium	0.05 mg/L	0.01 mg/L	0.01 mg/L	0.01 mg/L	0.01 mg/L	0.05 mg/L
Silica Dioxide			10 mg/L	No Standard		
Silver	0.1 mg/L[7]	0.05 mg/L	0.01 mg/L	No standard	No standard	

Table 6 Comparison of International Drinking Water and FDA Bottled Water Guidelines* (continued)

Parameter	USEPA** Maximum Contaminant Level (MCL)	Canada*** Maximum Acceptable Concentration	EEC**** Maximum Admissible Concentration	Japan***** Maximum Admissible Concentration	WHO****** Guideline	Bottled Water U.S. Federal Drug Administration Level
Solids, total dissolved	500 mg/L[7]	500 mg/L	No standard	500 mg/L	1000 mg/L	
Sodium			75-150 mg/L	200 mg/L	200 mg/L	
Sulfate	250 mg/L[7]	500 mg/L	250 mg/L	No Standard	250 mg/L	
Turbidity	0.5-5 NTU	1 NTU	4 JTU	1–2 units	5 NTU	<5 NTU
Zinc	5 mg/L[7]	5.0 mg/L	No Standard	1.0 mg/L	3.0 mg/L	

* To our knowledge, data in this table were accurate and current at the publication date. Contact the regulatory agency in your area for the most current information.

** United States Environmental Protection Agency.

***These limits are established by Health Canada.

****In the EEC (European Economic Community), these limits are set by the European Committee for Environmental Legislation.

*****In Japan, these limits are established by the Ministry of Health and Welfare.

******World Health Organization.

*******U.S. Secondary MCL.

********Identified as a parameter to be regulated in the future.

*********Threshold Odor Number.

3.7.1 Definitions of USEPA Approved and Accepted

USEPA Approved

The United States Environmental Protection Agency (USEPA) establishes limits for maximum contamination levels of certain constituents in water. It also requires that specific methodology be used to analyze for these constituents. Sometimes the USEPA develops these methods; more often, the USEPA evaluates methods developed by manufacturers, professional groups, and public agencies such as:

- American Public Health Association
- American Water Works Association
- Water Environmental Federation
- American Society for Testing and Materials
- United States Geological Survey
- Association of Official Analytical Chemists

When a method meets the USEPA criteria, it is *approved.* All USEPA approved methods are cited in the *Federal Register* and compiled in the *Code of Federal Regulations.* USEPA-approved methods may be used for reporting results to the USEPA and other regulatory agencies.

USEPA Accepted

Hach has developed several procedures that are equivalent to USEPA approved methods. Even though minor modifications exist, the USEPA has reviewed and accepted certain procedures for reporting purposes. These methods are not published in the *Federal Register,* but are referenced to the equivalent USEPA method in the procedure.